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VACUUM

Application of Vacuum Process Evaluation to the Study of Outgassing

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A systematic quantitative method of analyzing vacuum processes is presented. This method is especially suited to determining the outgassing occurring within a vacuum system as a continuous function of time and analyzing the resulting data to obtain information as to the source and nature of the outgassing. The technique and its application in determining the optimum combination of such parameters as temperature, time, materials, restrictions and pumps on such processes as hermetic volume exhaust and cellulose dehydration are described. Vacuum process evaluation techniques are used to study such phenomena as the outgassing characteristics of insulating materials and vacuum gauges, the flow of gases through orifices and short tubes, and the gettering action of materials. The method has been programmed for digital computer solution and is a rapid and inexpensive way to analyze some vacuum engineering problems.

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Introduction

A new technique has been developed to study the nature of outgassing in vacuum systems and the effect of certain parameters such as pumps, tubulations, and temperatures on the outgassing process. We call this technique Vacuum Process Evaluation[1, 2]. It is an application of vacuum engineering to produce a method which will : (1) Determine the outgassing occurring within a vacuum system as a continuous function of time, and (2) Analyze the resulting data to obtain information as to the source and the nature of the outgassing. This technique has been used to study many different types of vacuum engineering problems dealing with outgassing and gas flow.

By " outgassing " we include all forms of gas entering the gaseous phase from the liquid or solid phase. This gas may be adsorbed, chemisorbed, or it may originate from evaporation, decomposition or from surface porosities. In many vacuum applications outgassing may be originating from any or all of these sources and in addition it may include several gas types from different material sources.

The outgassing curve

When a vacuum system is being exhausted in the absence of outgassing, the pressure versus time can be accurately predicted from a knowledge of the pumping speed of the system and the volume. When outgassing is present, the pressure versus time does not follow the prescribed curve. This difference in the rate of change of pressure is a direct measure of the outgassing, and hence can be used as a method for obtaining the outgassing curve.

If a volume V is being continuously exhausted by a pumping system of known throughput, Q, and also contains some outgassing or virtual leak, L, we can write the differential equation

$$L = Q + V\mathrm{d}P/\mathrm{d}t. \tag{1}$$

L is the gas flow into the volume and may be a function of time, temperature, and pressure. Q is the total gas flow out of the volume and is a function of the gas type, temperature, and pressure. $V\mathrm{d}P/\mathrm{d}t$ is the net gas flow out of the volume, or the difference between L and Q. For any pumping system, the relationship between pressure and throughput can be determined for a particular gas and temperature condition. This can be obtained from the equations governing the flow of gas through restrictions or by direct measurement either with calibrated leaks or from the pump down in the absence of outgassing. The last method will be discussed later.

Unless the pumping system is exceedingly slow or the volume quite large, it will be observed that after an initial period of pumping, the rate of pressure decay will decrease. At this point the $V\mathrm{d}P/\mathrm{d}t$ part of equation (1) becomes very small relative to Q. As a result, frequently $V\mathrm{d}P/\mathrm{d}t$ is ignored and it is assumed that $L = Q$. There are two disadvantages to this. If the change in the outgassing rate is of the same order as the normal pump down rate, then the resulting data will be highly inaccurate. Hence, fast outgassing processes cannot be studied. The second objection is that the initial outgassing data during pump down is lost, and it is generally difficult to know at which point in the pump down the approximation can be considered valid.

An advantage of including the VdP/dt part of the equation is that if anything occurs to increase the pressure momentarily, such as a transient leak, the analysis is still valid. The resulting outgassing curve will be continuous except for a pip at the instant that the transient leak occurred.

These effects are illustrated in Fig. 1. Curve A is the outgassing curve obtained from the simplification that

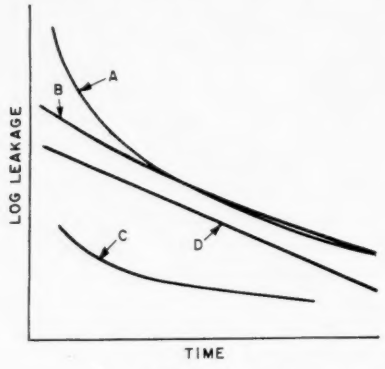

FIG. 1. Outgassing curves.

$L = Q$. Curve B corrects for the $V\,dP/dt$ effect of the gas being removed from the volume. Curve C is the separate system outgassing for similar initial starting conditions but with the material absent. Curve D is the final corrected curve for the material after subtracting the system outgassing.

The value of the leakage which is obtained from equation (1) represents all outgassing within the system including the pump limitations. Frequently it is desired to study only a part of the total outgassing, for example the outgassing of a material in a chamber. In order to obtain this data it is necessary to measure separately the outgassing of the empty chamber as a function of time. This outgassing is then subtracted from that computed from equation (1). It is another frequent practice to ignore the change in the outgassing of the system and merely subtract a constant value of system outgassing, proportional to the ultimate pressure of the pumping system. Unfortunately, even if the system outgassing is accurately measured for what would appear to be identical conditions to those to be used during an outgassing test, there is no easy way to determine the effect of the outgassing of the materials on the system outgassing. Hence there is always a question as to the accuracy of the correction being applied for the system outgassing. Note that the system calibration of Q vs. P cannot be combined with the system outgassing curve because the first is a function of pressure and the second is predominantly a function of time. If it is desired to obtain the separate outgassing of several different types of gas, the partial pressure of each must be obtained as a continuous function of time with some form of gas analysis equipment such as a mass spectrometer. The calculations are then carried out for each separate gas.

Frequently, particular types of outgassing can be recognized from the shape of the curve when plotted on particular coordinates. For example, an idealized adsorption degassing from a single valued energy site will yield an outgassing curve which is a straight line when plotted as the logarithm of the outgassing versus linear time. A diffusion type outgassing from a flat surfaced material of initially uniform gas content will yield a straight line with a 2 to 1 slope when plotted on log-log paper, up to the point that the diffusion gradient penetrates to the center or far side of the material, depending on whether the material is completely within the vacuum or represents one of the walls. When two different outgassing processes are occurring simultaneously, it is possible to graphically reduce the total outgassing curve into its two different constituents.

A limitation of the outgassing curve is that curves may be obtained which are not easily identified, or data for the outgassing of two different materials may be obtained which are similar but obviously not the same mathematical relation. Further analysis, as indicated below, is then required in order to interpret the outgassing curve.

Total gas curve

The second curve which has been used for studying outgassing is that of the total gas evolved as a function of time. This is obtained from the equation

$$\Sigma G = \int_O^T L\,dt \tag{2}$$

where ΣG refers to the total gas given off from time equal zero to the time at which the point is plotted. The total gas evolved is frequently a simple mathematical function of time and as such can be recognized from a plot of total gas versus time. Normally the best analysis can be obtained by using a log-log plot for this curve. One limitation is that the shape of the curve depends on having complete data from time zero. Unfortunately, a portion of the initial outgassing is lost due to the fact that some period of time is required to exhaust the system from atmospheric pressure to the point where outgassing can be measured. This can be overcome in part by using a fast initial exhaust.

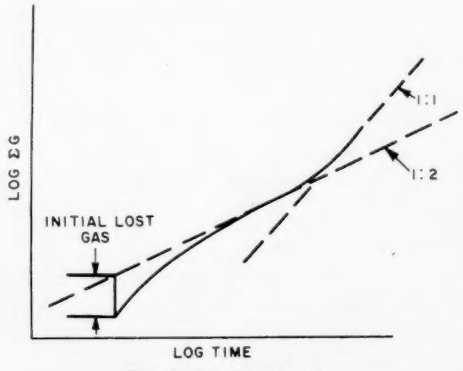

FIG. 2. Total gas curve.

Fig. 2 illustrates the application of the total gas curve for analysis. This graph represents the total gas evolved from a cellulose sample at 150°C on a log-log plot. The error due to the lost initial gas is apparent on the extreme left of the

curve. As time progresses, this error becomes negligible and the curve tapers into a 1 : 2 slope characteristic of a diffusion type reaction. As the diffusion outgassing decays, we note that the curve makes a transition into 1 : 1 slope. This is indicative of a decomposition reaction where the outgassing is constant.

In many instances the outgassing curve and the total gas curve are insufficient for interpreting the process, and a further method of analysis is desired.

The half life curve

The concept of half life has been used in many engineering technologies as an aid to analysis. Its adoption into the field of outgassing should not then be surprising. The difficulty encountered is in defining what is meant by the half life. At first encounter it would be expected that the half life would be the time to reduce the outgassing by a factor of two. Because of the changing nature of outgassing, it would not be possible to evaluate such a half life until the outgassing had actually decreased to half its value. Then at what instant of time would it be applied? Rather than the time to reduce the actual outgassing by a factor of two, what is required is the time to reduce the tangent to the outgassing curve by a factor of two. This we define as the instantaneous half life. Due to the exponential decay of many outgassing processes, and to be consistent with the normal definition of half life, the tangent to the outgassing curve is taken as the logarithmic tangent. The equation for the half life can be derived as

$$T_{1/2} = 2.3\ \mathrm{d}t/(d \log L). \tag{3}$$

Graphically the half life can be obtained by drawing a tangent to the curve of the logarithm of the outgassing versus linear time. The time for this slope to decrease by a factor of two is then equivalent to the half life.

The half life has a number of advantages over the other curves in the analysis of outgassing data. Since the half life is not an accumulative function, as is the total gas curve, the effect of initially lost gas does not interfere with the analysis. A further advantage is that the slope of a curve is more sensitive to slight changes than the original curve. Of course this is also a disadvantage, for if slight errors are present in the outgassing curve, these are amplified on the half life curve. As a result more care is required, but considerably more data are obtained. Generally, the half life curve is plotted as a log-log function of time. The major advantage of the half life curve is that it can be used to study the effect of various parameters on the outgassing curves. For example, consider Fig. 3 which shows two outgassing curves. One is for a fixed quantity of cellulose paper insulation, loosely packed within a vacuum system. The second curve is for the same quantity of cellulose wound tightly in the form of a capacitor roll. The outgassing curves appear fairly similar, yet there is obviously some difference. Fig. 4 shows the half life curves for these two outgassing processes. The unrolled sample has a half life which is a linear function of time as evidenced from the straight 45° slope of the half life curve. The rolled sample however starts out on a displaced 45° line, then after a period of time it transists back to the 45° line of the unrolled sample. The interpretation of this is that the winding tightness of the rolled sample interfered with the free outgassing of the paper. In fact, the amount of displacement between the two curves is a direct indication of the effect of the winding tightness on the process.

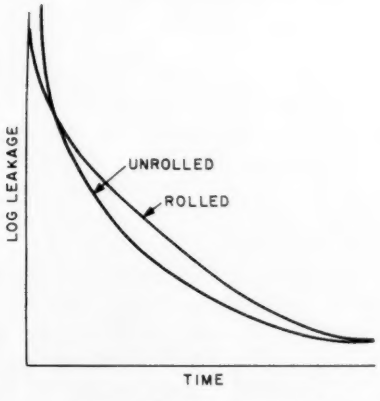

FIG. 3. Cellulose outgassing.

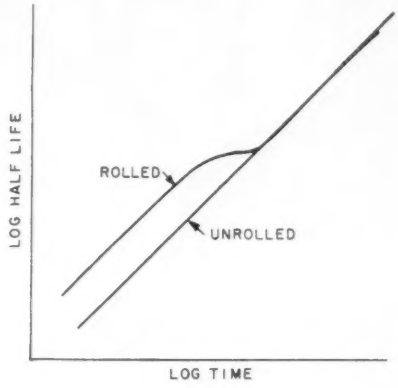

FIG. 4. Cellulose half life.

In similar fashion the half life curve has been used to study the effect of tubulations, pumping ports, systems, and temperature effects on particular outgassing processes. The half life curve is also an advantage in breaking up a complex outgassing curve into its various constituents. This is illustrated for a simple case in Figs. 5(a) and 5(b) for the outgassing of two different insulating materials. The two curves show some degree of similarity. The half life curves, however, are quite different. One of them is a straight line suggestive of a diffusion type outgassing, the other has one horizontal line changing over to a second horizontal line. This latter half life is suggestive of two surface reactions proceeding in parallel. This could be due to two different gases, or the same gas coming from two different binding energy levels.

The effect of a limited speed pumping system on the outgassing process can sometimes be anticipated by comparing the half life of the vacuum system to the half life curve obtained in the analysis. If the system is not capable of removing the gas fast enough to keep the pressure well

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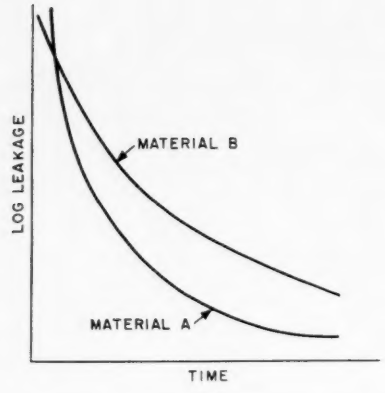
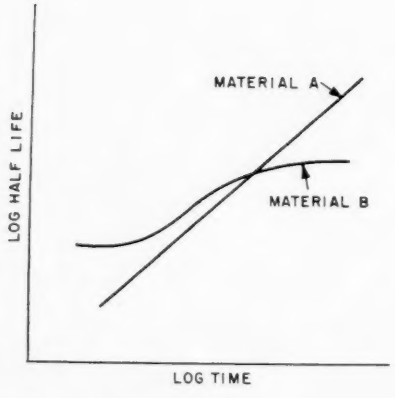


(a)



(b)

FIG. 5 (a and b). Outgassing of insulating materials.

ahead of the outgassing, the residual pressure will slow down the outgassing process. Such a limitation can be suspected whenever the process half life is lower than the system half life. The system half life is defined as the time to reduce the pressure in the volume by a factor of two at the instantaneous rate of change of the pressure and in the absence of outgassing. This can be shown to be equal to

$$T_{1/2} = 0.693\ V/S \tag{4}$$

where S is the speed of the system at the value of pressure that the volume would have at time t during a normal pump down. In Posiuielle viscous flow where the speed is a linear function of pressure, the half life is a linear function of time. In molecular flow both the speed and the half life are constant. Fig. 6 illustrates a typical system half life curve.

The criteria of comparing the system half life to the outgassing half life is only a one way street. If the process half life is the smaller, system effects can be expected because the system will eventually attempt to slow down the process to its own half life. If the process half life is greater, this does not exclude system limitations. This is true because an initial outgassing may be at a very high rate, too fast for the pumping system to handle, and yet have a relatively slow rate of change or large half life. In this event, the system will slow

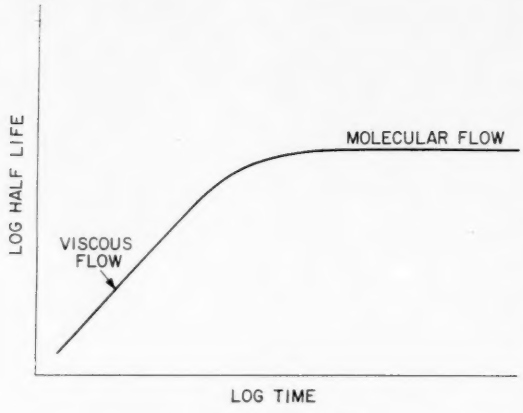


FIG. 6. System half life.

down the outgassing, but since it is already slower than the system, no indication is evident from a simple comparison of the system half life to the process half life. In fact, the system must always have some finite effect on the outgassing even though it is too small to be measured. An extreme example of this is that of evaporation from a liquid surface at constant temperature. In order for the system to have negligible effect on the evaporation, the equivalent molecular orifice area of the pumping system must be very large relative to the evaporating area. The relation $[1-A/(A+A')]$ defines the efficiency of the evaporation rate, where A is the evaporating surface area and A' is the orifice area which would have the same speed as the pumping system. In this process the half life of the evaporation is infinity, which is obviously greater than any system which may be pumping on the material. Yet if the system is not sufficiently fast, regardless of what its half life is, it will limit the evaporation. The best method for checking system, pumping port or temperature limitations is to deliberately change the parameter in question and determine if the change has any effect on the half life. The same process will be identical in any system which is not limiting. In practice we have several times proved that a particular tubulation was not limiting the process by taking the pressure–time curve with and without the restriction present. Even though the resulting pressure curves were different, the outgassing and half life curves were identical. In other instances a definite change was observed, especially in the half life curve, indicating exhaust port limitations.

To further illustrate the value of the half life in the analysis of outgassing curves, let us consider a different type of reaction, that of absorption or diffusion. In Fig. 7(a) we have illustrated the cross-section of a piece of material containing a gas in solution. When a vacuum is applied to one side of the wall, outgassing occurs and a diffusion gradient forms within the material. As time passes, the gradient moves deeper into the material and the outgassing decays as shown. Note, however, that in this case we do not obtain a straight line on a plot of the log of the leakage versus time (Fig. 7b). If we compute the instantaneous half life along the curve and then plot the log of the half life versus the log of the time, we obtain a 45° line indicating

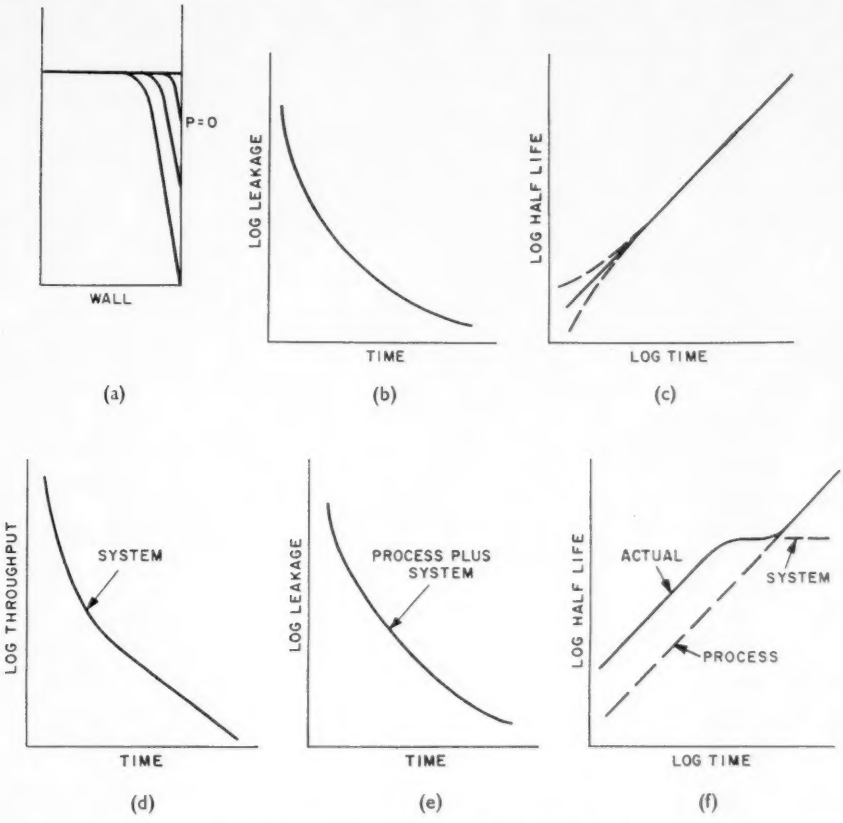


FIG. 7 (a–f). Absorption or diffusion outgassing.

a linear relation between the two (Fig. 7c). Depending upon non-uniform gradients or errors in the reference zero time, the lower end of the curve may deviate from a straight line as illustrated by the dashed lines. This can be used to study the effect or presence of previous outgassing processes. In Figs. 7(d), (e) and (f) we illustrate the effect of system limitations. Fig. 7(e) shows the actual outgassing curve which may be obtained in a given case when a diffusion type reaction is taking place in a material within a vacuum system. The curve looks very similar to the one in Fig. 7(b). Yet when the half life curve is computed and plotted (Fig. 7f), it is easy to see the effect of the system limitations. In this type of reaction the system is generally limiting early in the outgassing while the diffusion is limiting at the end.

Evaluation of system pumping speed

In order to obtain the outgassing curve, it is necessary to know the accurate relation between the pressure and the system throughput. Normal pumping speed curves of pumps are not sufficiently accurate due to variations between pumps and temperature effects. Even an accurately calibrated diffusion pump cannot be relied on to give constant speed. As a result, it is necessary to deliberately limit the speed of the pump by a series resistance which can be relied on to remain constant. This poses the problem of how to measure the pumping speed of the net system. If the dimensions of the restriction are accurately known, it is possible to compute its conductance. Otherwise it must be measured. Calibrated leaks can be used for that portion which is in molecular flow where the speed is constant. At higher pressures it would require a large number of such leaks to obtain a satisfactorily accurate curve. An alternate method is to use the well-known constant volume calibration method where the throughput is evaluated from equation (1) for the condition that L is equal to zero. The difficulty is in truly making L equal to zero. We have found in practice that

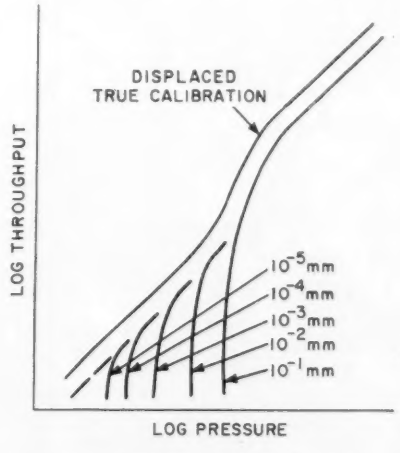


FIG. 8. Pumping speed calibration.

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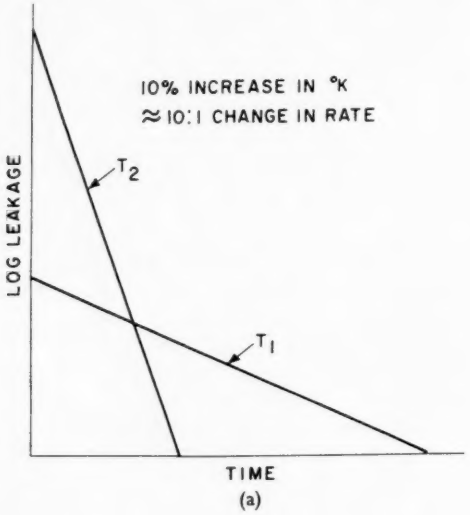
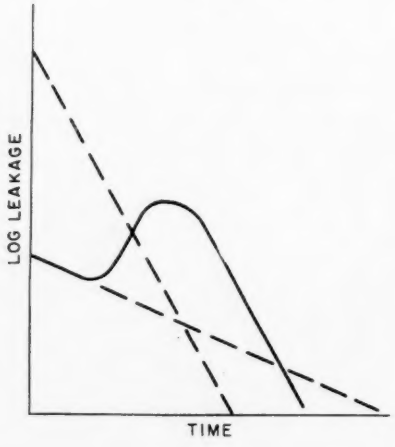
even after the system has been pumped for a long period of time and is relatively clean, once gas is introduced, a short term high level of outgassing will always result. This problem can be overcome by raising the pressure only slightly above the equilibrium and then taking a pump down. This is then repeated for higher and higher levels of initial pressure, eventually reaching atmosphere. For example, on a system with a normal ultimate pressure of 10^{-6} Torr, the pump down will be taken first from 10^{-5} Torr and then successively from one decade higher increments. A typical combination of the family of curves is shown in Fig. 8. The upper envelope represents the true system calibration. From this true calibration and the other separate curves, the system outgassing for the different exposures can be obtained if desired.

The effect of temperature

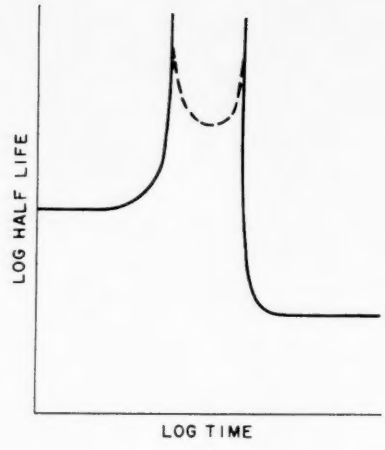
We have observed that, for most outgassing processes, and in fact for most all reactions from solid or liquid phase to gas phase, a 10 per cent increase in *absolute temperature* will result in approximately a ten-fold reduction in the half life (see Fig. 9a). This is similar to the chemist's rule of thumb for first order reactions that a 10 °C change will double the rate. By using the percentage relation, the rule is valid over a much broader span of temperature. For example, the vapor pressure of metals at elevated temperature will fit this generalization. As an example of the importance of this temperature dependency, we can consider the condition of adsorbed water. At room temperature, the half life of adsorbed water on many materials is approximately 1 hr. By simply raising the temperature to 90 °C, the half life will be reduced to about one half minute and rapid surface clean-up can be obtained. When the temperature changes from one value T_1 to a second T_2, we obtain the type of curve shown in Fig. 9(b). As the temperature increases, we see an increase in outgassing which eventually begins to decay as the surface becomes depleted. When temperature equilibrium is reached, the outgassing curve will again follow a log function as shown. The half life of such a reaction is illustrated in Fig. 9(c).



(a)



(b)



(c)

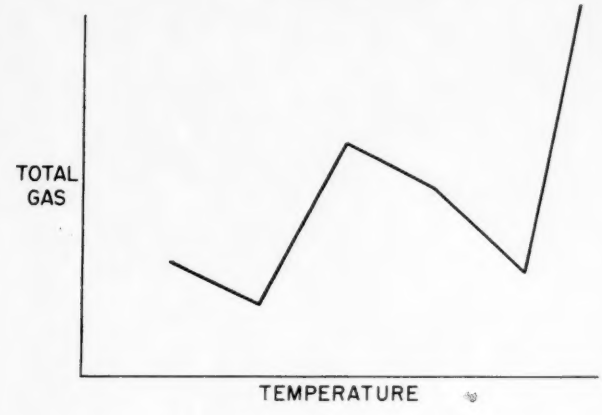
FIG. 9 (a–c). Temperature dependency.

As the temperature increases, the half life will decrease only to that point where it is limited by the system restrictions. Further increases in temperature will fail to have any important effect on the outgassing. Rather, the pressure will be almost in equilibrium with the surface and the process will be limited by how fast the gas is removed from the volume.

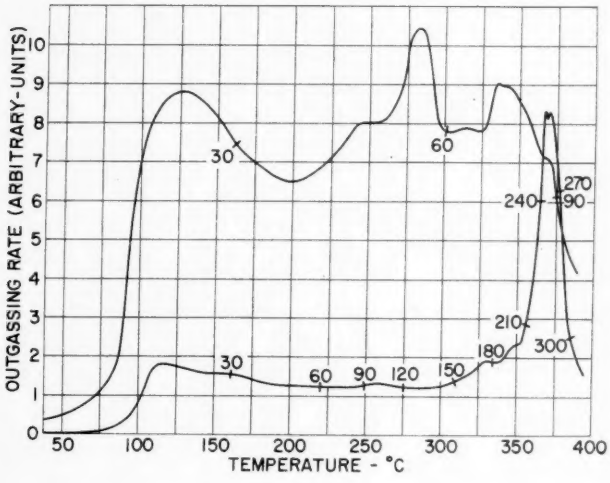
Complex material outgassing

One of the most recent applications has to do with those situations where a complex surface or material is involved. One example of this can be obtained by reference to the work published by Dr. B. Todd[3, 4] on the outgassing of glass surfaces. Dr. Todd states that the levelling effect of the outgassing at different temperatures suggests a complex hydrate structure on the surface. From his data, we can calculate the instantaneous outgassing and its half life. The 150° curve, for example, shows a constant half life of approximately 2 hr. Considering the 10 per cent per decade temperature dependency referred to earlier, an increase of only approximately 40 degrees is required to reduce this half life by 10 : 1. Hence, at higher temperatures this particular component will outgas quite rapidly.

Previous work on glass outgassing has generally been reported on the basis of temperature dependency. Fig. 10(a)



(a)



(b)

FIG. 10 (a and b). Outgassing of glass.

is a typical curve of the temperature dependent glass outgassing similar to those found in Dushman's *Vacuum Technique*[5]. To obtain this type of curve, the total gas is collected over a long period of time at each temperature. Hence, each point represents an integration of all sources of outgassing over that period of time.

In view of the high temperature dependency, the anticipated complex structure, and the limited gas in each chemisorbed state, we can speculate what the outgassing would be like if measured as a continuous function of time while the temperature is increasing. As the temperature increases, the half life of all members of the complex surface should decrease and one by one they should reach a value where their particular outgassing is fast and their half life is of the order of magnitude of the measuring time. This is followed by depletion of the particular member and a resultant decay in the outgassing curve till the next member reaches a sufficiently low half life. Such a curve should result in a "finger-print" of the particular glass being studied. By studying different glass compositions, it should be possible to identify the different sources of the hydrate breakdown. If a particular batch of glass has been identified, the degree of hydration can be measured by comparing the outgassing curve of a test sample to that of a completely hydrated sample. This could also be used to study the rate of formation of the different hydrates.

To test this speculation, two different samples of Pyrex glass were outgassed. Both samples had been in the glass shop for unknown periods of time. Fig. 10(b) shows the results of the tests. The rate of heating is indicated by the time marks on the curves. The first sample was heated at a very slow rate. It is interesting to note that the outgassing level was relatively low up to 350°C. At this temperature a very large quantity of gas was evolved. From the time scale we note that we were on this peak for almost one third of the heating cycle.

A much faster heating cycle was used for the outgassing of the second sample. The most outstanding difference is the much larger, low temperature outgassing. The difference between these two serves to illustrate the importance of knowing the past history of a sample prior to taking outgassing data.

Many other possibilities exist in utilizing a controlled temperature change. For example, it may possibly be used to identify complex fuels or lubricants on the basis of their vapor pressures. Curves similar to the one shown for glass should result. It also may be possible to use this approach to aid in the study of complex decomposition reactions.

Digital computer and data reduction

In the analysis previously discussed, it is apparent that a considerable amount of work is required to obtain a complete family of curves for only a single outgassing sample. First the pressure time curve is obtained and then the following operations are required at as many as 100 points : Correct pressure curve from calibration data, convert corrected pressure to equivalent pressure in volume if measured remotely, draw slope of pressure time curve, compute $V\,dP/dt$, look up value of Q at selected value of pressure, take difference, look up system outgassing at value of time for which pressure was selected, take difference, plot one point on the outgassing curve, integrate by taking average value of last two outgassing values times the differential time and add to previous total gas. After the outgassing curve and total gas curve are obtained, another 100 slopes to the outgassing curve may be required to obtain values of $d \log L/dt$ for computing the half life curve. This sort of routine calculation is ideally suited for a computer. In the course of obtaining an ideal computer program, seven different programs were written. The last of these was essentially a combination of all the others. The complete computer routine is far too complex to be presented in this report. However, a simplified flow diagram and the associated equations may be helpful to someone who would like to set up their own program.

The basic philosophy of the program is that each point

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desired on the pressure time curve is punched out on a separate IBM card. An IBM 650 digital computer was used. As many cards are stored on the memory drum of the computer as are required for the particular solution being utilized. The answer card for one point is punched out at the completion of the single sequence of calculations. All stored data is shifted one position and an additional card is read in to replace one which is removed. The calculations are then repeated. The master program has a choice of three different inputs, three outputs, and four storage tables.

TABLE I

Outline of computer program

1.	$P_A = Y_{A/F}$	X_{A_1} Y_A = coordinates of a particular point on the pressure-time recording.
	$T_A = X_{A/F}$	F = counts per unit length of graph paper.
2.	$T_{1A} = KT_A$	K = sec/unit length of graph paper or conversion from min or hr to sec.
3.	$P_A \rightarrow P_{OA}$	Vacuum gage calibration from tables stored in machine and linear extrapolation.*
4.	$P_{OA} \rightarrow P_{1A}$	Pressure conversion from line to volume from tables and linear extrapolation.*
5.	$\Delta P_{1B} = P_{1B} - P_{1A}$ $\Delta T_{1B} = T_{1B} - T_{1A}$	
6.	$P_{1B'} = (P_{1A} + P_{1B})/2$ $T_{1B'} = (T_{1A} + T_{1B})/2$	averaging
7.	$P_{1B'} \rightarrow Q_{1B'}$	Determination of theoretical flow through system from tables and linear extrapolation.*
8.	$T_{1B'} \rightarrow L_{1B'}$	System outgassing—from tables and linear extrapolation.*
9.	$Q_{2B'} = \frac{1}{A}\left[Q_{1B'} - L_{1B'} + \frac{V_1(\Delta P_{1B})}{\Delta T_{1B}}\right]$	Outgassing per unit A. A may be area, volume or weight of sample.
10.	$\Sigma G_B = Q_{2B'} \cdot T_{1B} + \Sigma G_{(n-1)}$	Add on gas quantity to previous total.
11.	$m = (T_{1C'} - T_{1B'})/a$ $n = (T_{1D'} - T_{1C'})/a$ $Q_{2C''} = \frac{Q_{2C'} + mQ_{2B'} + nQ_{2D'}}{1 + m + n}$ $P_{2C''} = \frac{P_{2C'} + mP_{1B'} + nP_{1D'}}{1 + m + n}$	Curve damping to smooth irregularities before taking slopes for half life; a is a constant and depends on reading frequency.
12.	$T1/2 = -0.3010 \frac{(Q_{2D''} + Q_{2C''})\Delta T_{1D}}{2\,\Delta Q_{2D''}}$	Half life calculation.

*General formula for linear extrapolation given X_i occurring between X_a and X_b

$$Y_i = Y_a + \frac{(X_i - X_a)}{(X_b - X_a)} \quad (Y_b - Y_a)$$

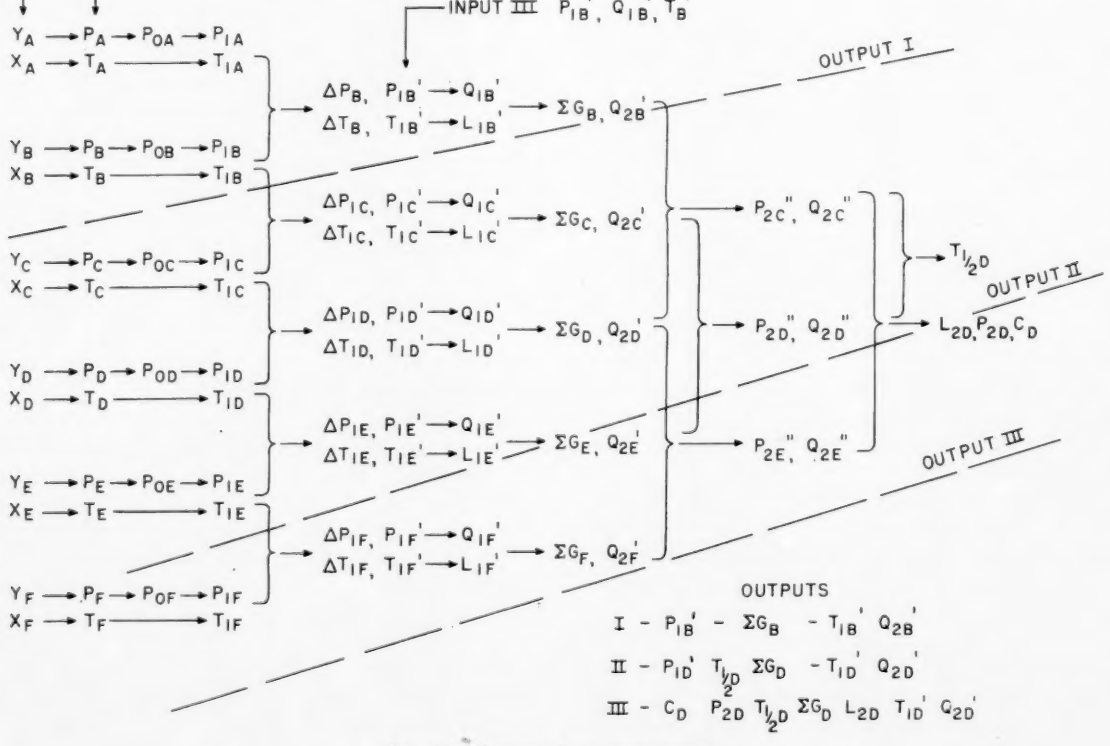
INPUT I Y AND X FROM DATA REDUCTION
INPUT II P AND T FROM TABULAR DATA
INPUT III P1B', Q1B', TB'
OUTPUT I
OUTPUT II
OUTPUT III
OUTPUTS
I - P1B' - ΣGB - T1B' Q2B'
II - P1D' T1/2D ΣGD - T1D' Q2D'
III - CD P2D T1/2D ΣGD L2D T1D' Q2D'

FIG. 11. Diagram of computer program.

The proper selection is governed by punching a control card. By proper punching of a second control card the individual outputs are presented as either linear or logarithmic answers in order to simplify the automatic plotting routine. Various other parameters, such as the volume, time or pressure conversion, and transfer cards to change a parameter or restart the summation, are all punched on individual cards which are stored. A general outline of the program is shown in Table I and Fig. 11. Note that output III adds three parameters which have not been discussed in this report. These parameters are still in the experimental stage, and involve a special solution to the two volume problem for simulation of changing temperature conditions during the outgassing. The speed of the computer depends on how many tables are involved and how many answers must be converted to logarithms. The average speed is 1 sec/series of calculations after reading in the program. A typical run of 100 points would require about 2 min.

Data reduction facilities represent another savings in cost. The individual pressure time points are punched directly from the strip chart recording by means of a data reader. This is composed of a pair of cross-hairs connected to counters and a parallel entry key punch. Cards are punched at an average rate of one card per second. The final answer cards from the computer are automatically plotted on standard plotting equipment. Average speed of plotting is better than one card/sec.

At first it appeared that the inclusion of the correction factors into the outgassing equation and the addition of the total gas curve and half life curve would represent considerable cost increase. By utilizing the computer program we now find that it is considerably less expensive to do a complete analysis with the computer than to do the simplest form of approximation by hand.

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Applications and problems

Any new computing or analyzing tool can best be evaluated in terms of its usefulness and the problems encountered in applying it. Vacuum process evaluation has been used to study such problems as the effects of various parameters on the dehydration of cellulose, the degassing and exhaust of electron tubes, the outgassing of various insulating materials, the flow of gases through tubes and orifices, calibration of vacuum gages, study of barium getters, and the complex surface outgassing of glass[1, 2]. In all applications it has been found to give highly reproducible results. To increase its value for studying material outgassing, we are presently building a high speed, ultra-high vacuum system with a built-in mass spectrometer.

There are many problems of applications which must be recognized in order to avoid erroneous or limited results. Most of these are inherent in any method of taking or studying outgassing data, and as such are a constant plague to the vacuum engineer. For example, during the initial pump down from atmospheric pressure, the gas flow is so large that the small outgassing cannot be observed. To minimize this time, a high speed initial exhaust system is desired. One of the final limits on the study of outgassing near the end of the process is caused by outgassing of the system from sources other than that being studied. The computer program allows the system outgassing to be measured and subtracted from the total outgassing, but when the outgassing of the sample is small relative to the system, large errors are introduced. The only answer to this problem is cleaner vacuum systems. For low level outgassing studies, organic materials must be eliminated and atmospheric contamination should be avoided.

Since most vacuum gauges are not absolute and depend on some property of the gas, the calibration of the gauge is always a serious problem. This is especially so if the composition of the outgassing is unknown. If the composition is changing, the errors introduced may well wipe out any benefits of using the complete outgassing equation rather than one of the simplifications. Whenever a single gauge is being used for studying outgassing, the values obtained are in equivalent nitrogen flow rates unless special calibration has been employed. The ideal solution for this problem is to use gas analysis and study each gas type separately.

Most all methods of studying outgassing depend on an accurate knowledge of the system pumping speed. Diffusion pumps cannot be relied on for such studies as they will have both short term pulsations and long term drift. This problem can sometimes be overcome by deliberately using a larger pump than is required and adding a series restriction which will not drift in calibration with time. Of course, such a restriction is still composition and temperature dependent. In studying fixed processes where the pumping system is part of the permanent equipment, it is sometimes necessary to use the diffusion pump unrestricted. In this event, care should be taken to calibrate the system and to maintain all variable parameters as constant as possible. This would include power, cooling water temperature and flow, and surrounding environmental temperature.

By far the most severe problem is that of temperature. Temperature changes confuse the analysis and affect the calibration of gauges, restrictions and pumps. In addition, the contraction of the gas flowing from a hot volume to a cold pump acts as an additional pump. Temperature changes should be avoided when possible, calibrated out if feasible, and carefully considered in the interpretation of the final analysis.

Conclusions

Vacuum Process Evaluation has been successfully applied to the study of many different types of vacuum engineering problems, predominately those of outgassing. Because of the addition of the parameter of the half life, a more detailed analysis is obtained and a better understanding of the outgassing process is realized. By using a digital computer, the resulting analysis is both less expensive and more accurate.

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The Vacuum Use of Molecular Sieves and other Desiccants

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The use of molecular sieve as a desiccant in vacuum systems has been investigated. A comparison of the water adsorption efficiency of the sieve, under static equilibrium conditions, with two other regenerable desiccants (silica gel and activated alumina) shows the sieve to be far superior. It is also shown that the non-regenerable desiccant phosphorus pentoxide, has a greater adsorption capacity than the molecular sieve. A comparison of the adsorption capacity of two column lengths of sieve under dynamic conditions is made, and the pressure differentials across the columns are investigated. The increase in the adsorption efficiency when the system is backed by an air ballast rotary pump is shown. Data are also given for moisture breakthrough, heat of adsorption, and regeneration times. As the sieve readily adsorbs air at atmospheric pressure, the time required for initial degassing is shown. An appendix describes a subsidiary water absorption test, made on a sample of phosphorus pentoxide, to show the progressive effect of surface deliquescence and relative vapour pressures.

Static tests

Experimental apparatus and procedure

The water adsorption efficiency of molecular sieve (type 4A, $\frac{1}{8}$ in. pellets) under static equilibrium conditions was determined by measuring its equilibrium vapour pressure at varying moisture contents. Similar information on samples

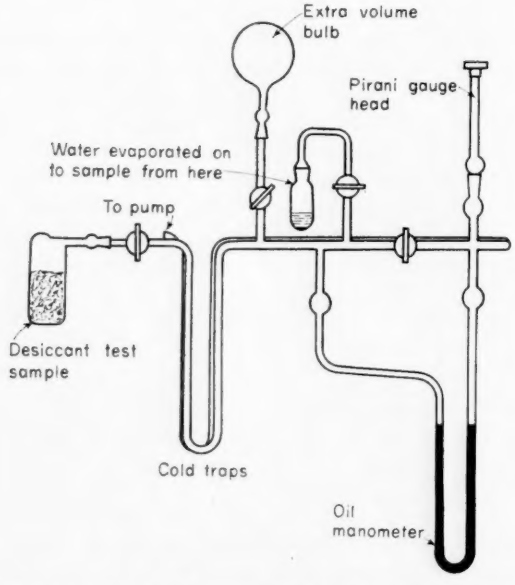


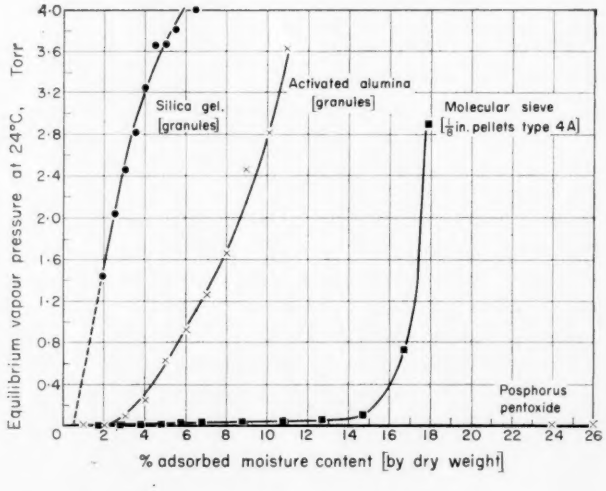
FIG. 1. Experimental apparatus for static adsorption tests.

of silica gel, activated alumina and phosphorus pentoxide has been obtained as previously published[1]. The general arrangement of the apparatus is shown in Fig. 1.

The test procedure was to evaporate successive known quantities of water on to the desiccant sample in a closed system, maintained at an air pressure of 0.02 Torr. At each stage, when equilibrium conditions were reached, the vapour pressure was measured by means of an oil manometer.

Results

Values of water vapour pressure up to 2.9 Torr and moisture contents up to 17.9 per cent by weight, were obtained, and a curve was plotted (see Graph 1). Similar curves for three



GRAPH 1

other desiccants : silica gel, activated alumina and phosphorus pentoxide, are shown as previously published using this method[1].

A comparison of these curves shows that under the static adsorption conditions, the percentage moisture contents of

the desiccants, exerting a water vapour pressure of 0.1 Torr are as follows :

TABLE I

Regenerable desiccants	Moisture content at 0.1 Torr (%)	Bulk density (lb/ft³)
Silica gel (granules)	0.9	42
Activated alumina (4/8 mesh)	3.0	45
Molecular sieve ($\frac{1}{8}$ in. pellets)	14.5	43
Non-regenerable desiccant		
Phosphorus pentoxide	>25 at 0.01 Torr	33

Dynamic tests

Experimental apparatus

The apparatus to find the water adsorption efficiency of the sieve under dynamic conditions was made completely

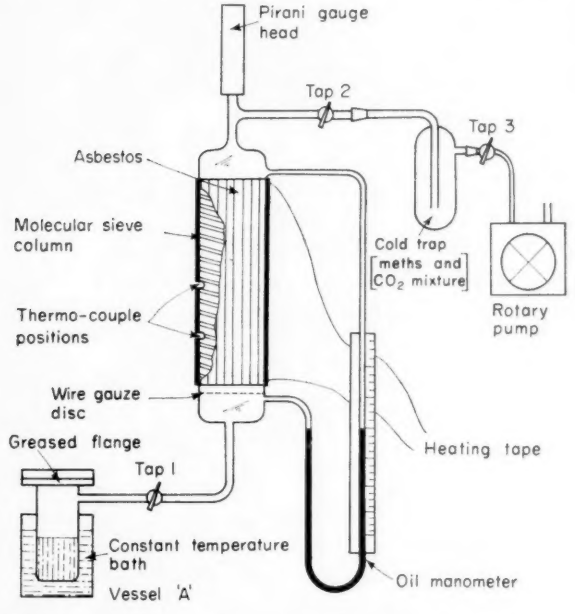


FIG. 2. Experimental apparatus for dynamic adsorption tests.

of glass, and was set up as shown in Fig. 2. A vessel containing water to be evaporated on to the sieve was connected to the sieve column inlet via tap 1. The column was wound with heating tape to enable the sieve to be regenerated *in situ*. The wall of the column was dimpled in two places, each dimple to house a thermocouple for temperature measurement during regeneration, and to measure the heat of adsorption of the sieve during the adsorption tests.

An oil manometer was placed across the column for absolute pressure drop measurements, and a Pirani gauge head was situated above the column to indicate the outlet pressure.

The column was connected via tap 2 to a demountable cold trap (−79 °C) which condensed moisture at breakthrough. The system was pumped via tap 3 by a two stage air ballasted mechanical rotary pump with a free air displacement of 20 l/min.

Experimental procedure

The column was first filled with molecular sieve (type 4A, $\frac{1}{16}$ in. dia. pellets) to the required height, the apparatus (see Fig. 2) was then evacuated with tap 1 closed and taps 2 and 3 open. A known quantity of water was placed in the vessel *A*, and the top flange was greased and replaced to form a vacuum seal. When the pressure in the apparatus reached 0.01 Torr, tap 1 was opened and the water in the vessel was progressively evaporated on to the sieve. The rate of evaporation (or water throughput rate) was dependent on the constant temperature bath, and was changed for each test. At the end of the test the quantity of water evaporated was determined by subtraction.

The moisture that broke through the sieve column was trapped out before reaching the pump. The trap was isolated by closing taps 2 and 3, and was removed at intervals without interrupting the test to enable the quantity of breakthrough water to be measured. To ensure the quick and complete removal of water from the warmed cold trap the inner surfaces were coated with a silicone fluid (i.e. Repelcote —a dilute solution of chlorisilane dissolved in carbon tetrachloride).

Throughout the tests record was made of moisture breakthrough quantities and change in sieve temperature. Also, readings were taken of pressure difference across the sieve using the oil manometer, and sieve column outlet pressures were noted by use of the Pirani gauge. Corrections made to the Pirani gauge readings due to the pressure of water vapour in the outlet pressure were found to be negligible in this instance. From these pressure readings, the sieve column inlet pressures were calculated.

Regeneration of the sieve was carried out *in situ* under vacuum. Tap 1 was closed and the column temperature was raised to 300 °C. The apparatus was simultaneously pumped and the liberated water vapour was condensed in the cold trap. The quantity of condensed water was measured at regular intervals as before, and as the amount of water adsorbed by the sieve in the previous adsorption run was known, the progressive " state of wetness " was determined.

Note : An approximate check on the dryness of the sieve during regeneration could be made by observing the outlet pressure on the Pirani, since a curve showing a rough relation between pressure and moisture content under these dynamic regeneration conditions had previously been obtained.

Results

Adsorption efficiency

Dynamic water adsorption tests were carried out as described above. The dimensions of the molecular sieve column were : length—13 in., diameter—$1\frac{1}{4}$ in. The sieve weighed 220 g and was in type 4A, $\frac{1}{16}$ in. diameter pellet form. Water adsorption efficiency was determined by the quantity of water adsorbed by the sieve at the time of breakthrough for a particular throughput rate. Breakthrough was indicated by a pressure rise on the outlet side of the column, and in all the tests, the time of breakthrough was recorded when this pressure (as indicated by the Pirani gauge) increased to 0.1 Torr. The results obtained are shown below in Table II.

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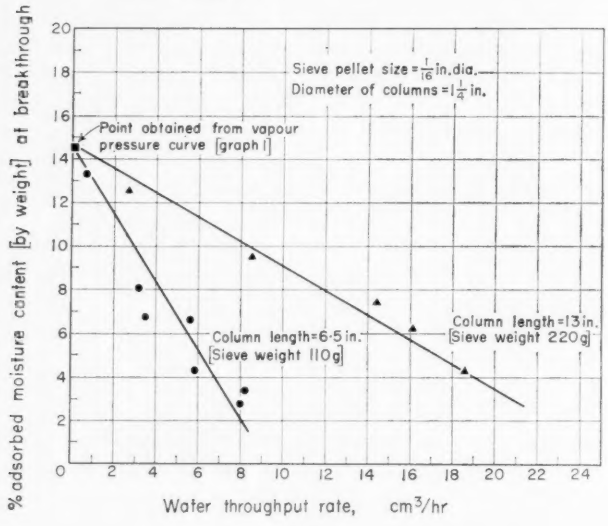
TABLE II

Water throughput rate (cm^3/hr)	($L\mu/sec$)	Time breakthrough occurred. (Pressure 0.1 Torr at column outlet)	% Moisture adsorbed before breakthrough
Nil	—	—	14.5*
2.63	0.69	10 hr 30 min	12.5
8.5	2.22	2 hr 27 min	9.5
14.4	3.78	1 hr 8 min	7.4
16.2	4.25	50 min	6.2
18.6	4.88	29.5 min	4.2

*Equilibrium value with sieve vapour pressure at 0.1 Torr, obtained from static vapour pressure test (see Graph 1).

A linear relationship was found between the percentage water adsorption, by weight, and the water throughput rate, and is shown in Graph 2.


% adsorbed moisture content [by weight] at breakthrough
Water throughput rate, cm³/hr
Sieve pellet size = 1/16 in. dia.
Diameter of columns = 1 1/4 in.
Point obtained from vapour pressure curve [graph 1]
Column length = 6·5 in. [Sieve weight 110g]
Column length = 13 in. [Sieve weight 220g]

GRAPH 2

Effect of column length on dynamic adsorption efficiency

To find the effect of the column length on the dynamic water adsorption efficiency, tests were made with a second sieve column : length—6½ in., diameter—1¼ in. The results

TABLE III

Water throughput rate (cm^3/hr)	($L\mu/sec$)	Time breakthrough occurred. (Pressure 0.1 Torr at column outlet)	% Moisture adsorbed before breakthrough
0.635	0.166	23 hr	13.3
3.12	0.818	2 hr 50 min	8.05
3.48	0.912	2 hr	6.7
5.6	1.46	1 hr 17 min	6.54
5.86	1.53	48 min	4.26
8.0	2.1	23 min	2.79
8.2	2.15	27 min	3.36

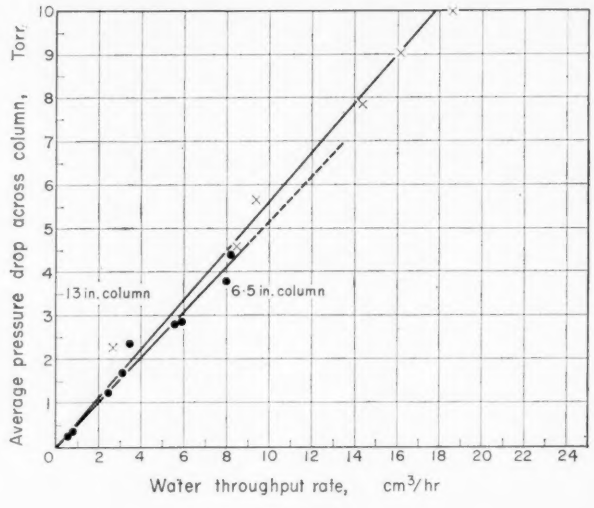
obtained are shown below as Table III, and are also plotted on Graph 2 for comparison.

The effect of column length on the pressure drop across it

Although only two column lengths (13 and 6.5 in.) were investigated it was still interesting to compare the effect of length on the column pressure drop at various throughput rates of water.

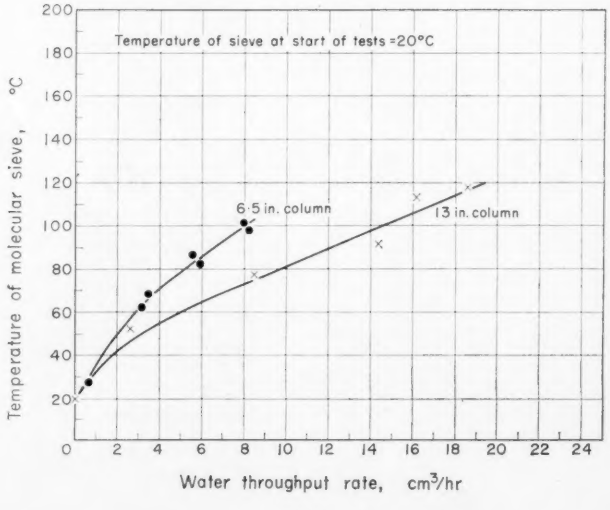
For this comparison to be made it was first necessary to calculate an average pressure drop, up to the breakthrough pressure, for each adsorption test. This average pressure drop was the difference between the average inlet, and the constant outlet pressures of the sieve. The latter was the existing residual air pressure, whilst the inlet pressure was the resultant of this air pressure, the pressure of the water throughput, and the vapour pressure of the lower surface of the sieve. This vapour pressure increased during the test as the moisture content of the sieve increased.

It will be seen from the results plotted in Graph 3 that the



GRAPH 3

pressure drop-throughput rate across the 13 in. column was only slightly greater than that across the 6.5 in. column, i.e. the difference in pressure drop for the throughput rates 1–6 cm^3/hr was 9 per cent.


Temperature of molecular sieve, °C
Water throughput rate, cm³/hr
Temperature of sieve at start of tests = 20°C
6·5 in. column
13 in. column

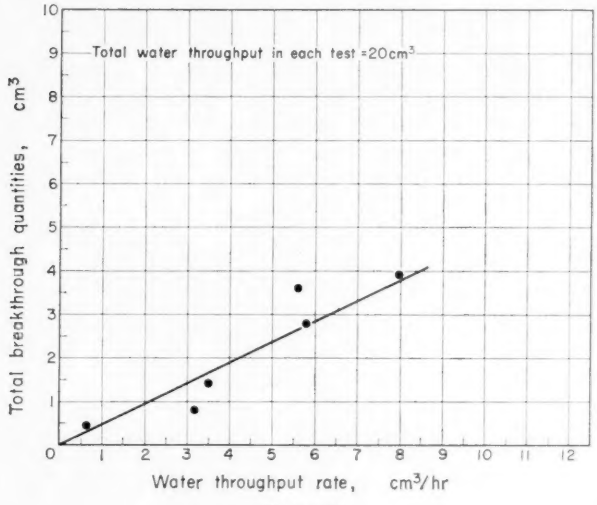
GRAPH 4

Temperature increase of sieve during water adsorption

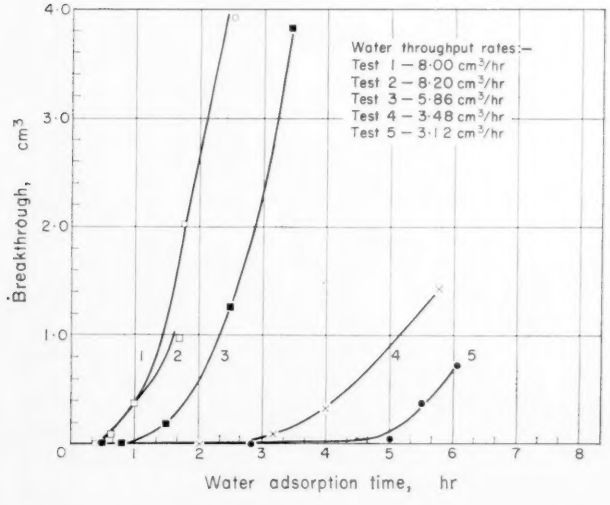
During the adsorption tests, the temperature of the sieve rose until breakthrough occurred. It then decreased by 20–40 °C until the end of the tests. The highest temperature reached by the sieve in each test has been plotted with corresponding water throughput rate (Graph 4). The temperatures reached by the sieve in the $6\frac{1}{2}$ in. column were higher than those in the 13 in. column for corresponding throughput rates.

Breakthrough quantities

In each of the adsorption tests on the $6\frac{1}{2}$ in. column, 20 cm^3 of water were evaporated on to the sieve column at the different throughput rates. The total breakthrough quantity in each case has been plotted with water throughput rate (Graph 5) and a linear relationship was found.



GRAPH 5


Water throughput rates:–
Test 1 – 8·00 cm³/hr
Test 2 – 8·20 cm³/hr
Test 3 – 5·86 cm³/hr
Test 4 – 3·48 cm³/hr
Test 5 – 3·12 cm³/hr
Breakthrough, cm³
Water adsorption time, hr

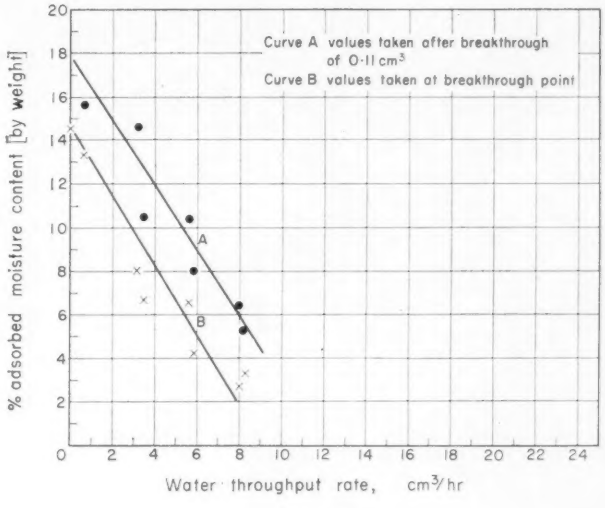
GRAPH 6

The relationship between the breakthrough quantities and adsorption times obtained during several tests is also shown (Graph 6).

Increased adsorption efficiency when backed by an air ballast rotary pump

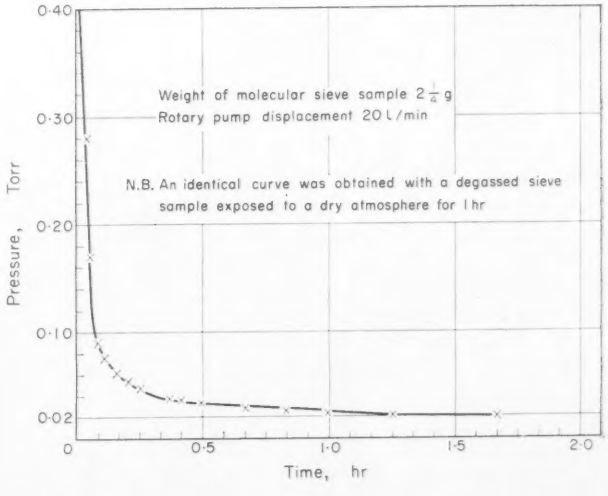
When the vacuum system is evacuated by an air ballast pump (i.e. a pump capable of pumping, efficiently, small quantities of water vapour) small breakthrough quantities can be tolerated during water adsorption by the sieve. Since this allows for a longer adsorption period, an increase in the sieve adsorption capacity results, the degree of which is related to the capacity of the air ballast pump.

Using a 110 g sieve sample, and assuming that a water breakthrough of 0.11 cm^3 is permissible, the adsorption capacity of the sieve at all water throughput rates is increased by 3.7 per cent by weight (see Graph 7).


Curve A values taken after breakthrough of 0·11 cm³
Curve B values taken at breakthrough point
% adsorbed moisture content [by weight]
Water throughput rate, cm³/hr

GRAPH 7

The limit to the adsorption capacity may then be the vapour pressure exerted by the sieve at a high moisture content, e.g. in equilibrium conditions a sieve sample with an adsorption of 14.5 per cent, by weight, exerts a vapour pressure of 0.1 Torr (see Graph 1).


Weight of molecular sieve sample 2¼ g
Rotary pump displacement 20 l/min
N.B. An identical curve was obtained with a degassed sieve sample exposed to a dry atmosphere for 1 hr
Pressure, Torr
Time, hr

GRAPH 8

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Initial removal of air from molecular sieve

When the sieve is placed in a vacuum system the air it contains is given off. From a typical pump down curve of a system containing a fresh 2¼ g sieve sample, and using a rotary vacuum pump with a displacement of 20 l/min it may be seen that a pressure of 0.1 Torr is reached in a few minutes, and the required 0.02 Torr in 1½ hr. This is shown in Graph 8. Thus when using a fresh sample of molecular sieve, or a sample which has been exposed to the atmosphere, this pre-pumping time must be taken into consideration.

It has been shown that small amounts of water drastically reduce adsorption of oxygen[2]. If, therefore, exposure of the sieve to the atmosphere after regeneration is unavoidable it may be desirable to terminate the regeneration leaving a small amount of residual moisture in the sieve.

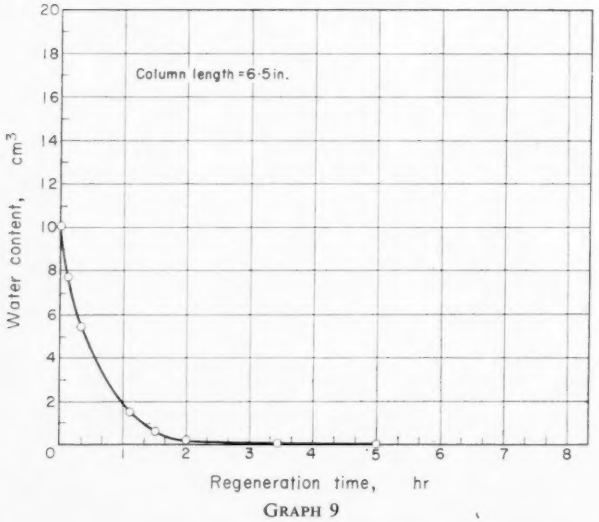
Regeneration

The times required to regenerate the sieve at 300 °C under the vacuum conditions previously described were found to vary with the quantity of sieve, and are tabulated below.

TABLE IV

Weight of sieve (g)	Approximate regeneration times (Original sieve moisture content >10% by weight)
36	1 hr 10 min
110	2 hr
220	4 hr

A typical moisture removal curve is shown in Graph 9.



GRAPH 9

The moisture content of the sieve as obtained in the previous adsorption run appeared to have no definite effect on the subsequent regeneration times.

For most practical purposes it is sufficient to reduce the moisture content of the sieve to 0.3 per cent, by weight, for in removing this final moisture content the regeneration time is increased by one third of the total time.

It was also found that when the moisture content of the sieve had been reduced to 0.3 per cent, by weight, and the temperature of the sieve was exactly 300 °C, the pressure (Pirani) at the outlet of the column was below 0.4 Torr. Thus regeneration was stopped when this pressure was reached.

It should be noted that at the start of the regeneration under vacuum, water vapour evaporated from the sieve at a very fast rate, and caused the sieve pellets to become violently agitated.

Discussion

The static adsorption efficiency of molecular sieve at a vapour pressure of 0.1 Torr has been shown to be much greater than silica gel and activated alumina. However, it has also been shown (Table I) that phosphorus pentoxide will absorb almost twice the amount of water than that adsorbed by molecular sieve, and still maintain a vapour pressure much lower than 0.1 Torr.

It may appear from this that phosphorus pentoxide is a superior desiccant for use under vacuum. This is true providing during absorption the exposed surface does not deliquesce sufficiently to form a covering layer of phosphoric acid. If the depth of the phosphorus pentoxide is greater than approximately 2.5 cm, the exposed surface becomes covered with phosphoric acid at around 25 per cent water absorption, by weight, trapping unused phosphorus pentoxide beneath it (this is shown by a subsidiary experiment as detailed in the Appendix).

The phosphoric acid surface continues to adsorb water, becomes diluted and very soon exerts a vapour pressure much above 0.1 Torr. Thus it is necessary for phosphorus pentoxide to have a large surface area with little depth if it is to attain a 25 per cent water absorption, by weight, whilst exerting a vapour pressure below 0.1 Torr.

It may also be noted that the phosphoric acid vapour formed during water adsorption by phosphorus pentoxide contaminates the desiccant chamber in which it is contained.

Conclusions

The molecular sieve was found to be a very efficient regenerable desiccant for use in a vacuum system. In static equilibrium conditions it can adsorb water up to 14.5 per cent, by weight, whilst exerting a vapour pressure of 0.1 Torr. Comparison with other desiccants per gramme weight, under static equilibrium conditions, showed that molecular sieve adsorbs sixteen times more water than silica gel and nearly five times more than activated alumina, whilst exerting a vapour pressure of approximately 0.05 Torr.

Under dynamic conditions the total water adsorption at breakthrough was found to be linearly dependent on the water throughput rate. The quantity of water adsorbed by 220 g of sieve (column length—13 in., dia.—1¼ in.) was increased from 4 per cent at 19 cm^3/hr water throughput, to 14 per cent at 1 cm^3/hr.

An increase in the column length from 6½ in. to 13 in. produced an increase in the adsorption capacity per gramme weight of the sieve. The increase varied with water throughput rate. Thus at very slow throughput rates, the effect was negligible, but as the rate increased the adsorption

capacity of the 13 in. column to the 6½ in. column increased, until at a rate of 8 cm³/hr it was five times greater. However the pressure drop was found to be slightly greater across the longer column (about 9 per cent) and therefore a maximum length should be determined, in order that the back vapour pressure exerted by the inlet surface of the sieve can be tolerated.

The quantity of water adsorbed by the sieve can be increased still further when the rotary pump used in the system is air ballasted to deal with small quantities of water vapour. The adsorption time would be lengthened until the rate of water breakthrough equalled the vapour pumping rate of the pump at normal pump temperature.

The heat of adsorption of the sieve was found to be quite considerable during the tests. At a water throughput rate of 8 cm³/hr the temperature of the sieve rose from 20 °C to 73 °C in the 13 in. column, and from 20 °C to 100 °C in the 6½ in. column.

When molecular sieve has been exposed to the atmosphere it is necessary to pump for approximately 1½ hr before a suitable vacuum is reached. This could be a serious limitation in a system where the moisture trap is open to the atmosphere for a period of time after regeneration.

Although it is usual to regenerate desiccants by passing hot air through the column, it was found more convenient in these tests to regenerate at 300 °C under vacuum, and so keep the sieve consistently free of adsorbed air.

Regeneration time was dependent upon the weight of the sieve and not upon the moisture content, and was found to follow the usual expotential drying law. Thus the 13 in. column containing 220 g of sieve required approximately 4 hr to regenerate whilst the 6½ in. column containing 110 g required about 2 hr.

The violent agitation of the sieve which occurred at the start of each regeneration run, should be taken into account when a drying column is designed.

Acknowledgements

My thanks are due to Mr. T. W. G. Rowe, head of the Drying & Distillation Research Div., for encouragement in this work, and to the directors of Edwards High Vacuum Ltd., for permission to publish this paper.

References

[1] E. M. Robson ; *Vacuum* **4**, 65 (1954).
[2] D. W. Breck *et al.* ; *J. Amer. Chem. Soc.* **78**, 7 (1956).

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APPENDIX

In order to determine the efficiency of phosphorus pentoxide in an air pressure of 0.02 Torr with relation to the state of the exposed surface, the following subsidiary test was made. A sample of dry phosphorus pentoxide (see Fig. A 1(a)) was allowed to absorb controlled amounts of water in stages. The vapour pressure and structure of the sample was noted at each stage.

These are shown diagrammatically in Figs. A 1(b–f). It will be seen from Fig. A 1(f) that the vapour pressure decreased when a fresh surface of phosphorus pentoxide was exposed.

Changes in sample structure during test

Diagrams showing percentage moisture absorbed, by weight, after the number of days the test was continued. (Time includes periods allowed for equilibrium conditions to be reached at 24 °C.)

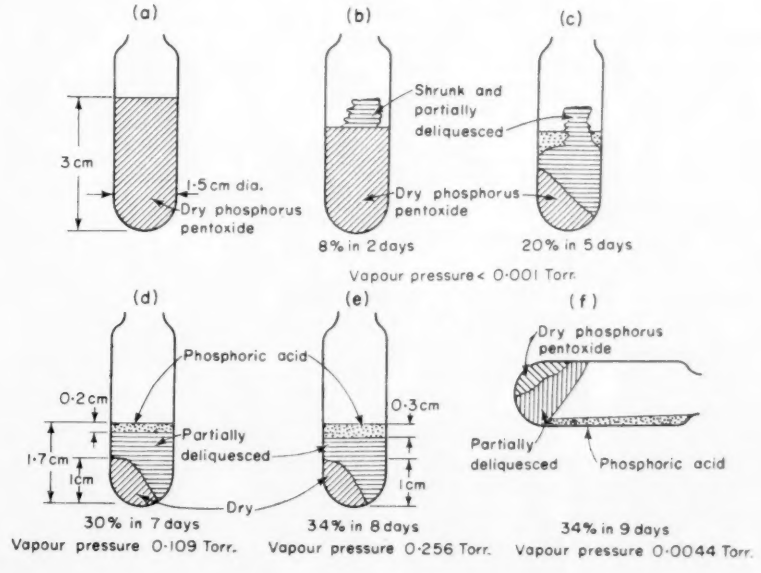

Fig. A 1

The Pumping of Nitrogen by a Bayard-Alpert Ionization Gauge in an Ultra-high-vacuum System

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(Received 14 April 1960)

The pumping speed for nitrogen of a Bayard–Alpert ionization gauge was measured in an ultra-high-vacuum system with pressures between 10^{-9} and 10^{-7} mmHg. The highest pumping speed measured was 2 l/sec, mainly chemical or non-electronic. After about 10^{15} molecules of nitrogen had been pumped, the chemical pump had decayed leaving the pumping speed about 0.25 l/sec, almost entirely electronic, at 8 milliamperes electron current. This speed was approximately constant until nearly 10^{17} molecules had been pumped, when a major decline in electronic pumping speed was observed. There was no measurable re-emission of chemically pumped nitrogen, and the re-emission probability of electronically pumped nitrogen was 10^{-6} to 10^{-5}/sec about 1 hr after completion of pumping. It is concluded that the main mechanism contributing to chemical pumping is the formation of a second adsorbed layer on the metal parts of the gauge, in particular the grid.

1. Introduction

An ionization gauge used to measure pressure also pumps the gas in the system[1, 2]. The rate of pumping, through the pumping speed, depends upon how much gas the gauge has previously pumped. Further, some of the molecules pumped may be re-emitted at some later time[3]. Thus an ionization gauge is both a sink and a source for gaseous molecules with the net effect depending on particular circumstances. Many physical phenomena, for example chemisorption and physisorption, may also be analysed as sinks and sources for gaseous molecules, and it is important when using an ionization gauge for the investigation of these phenomena to assess the relative contribution of the sinks and sources of the gauge. In the work of Becker and Hartman[4] on the chemisorption of nitrogen on tungsten the effect of the gauge processes on the observations was minor. However, in the measurements of Hobson[5] on the physical adsorption of nitrogen on Pyrex at very low pressures, this condition was not satisfied. In order to interpret the physical adsorption data unambiguously it was necessary to obtain at least a semi-quantitative knowledge of the behaviour of the gauge processes at very low pressures. Measurements of the pumping of nitrogen in ionization gauges have been reviewed by Alpert[6]. These measurements have been concerned mainly with electronic pumping at relatively high pressures and have not examined re-emission and chemical pumping in any detail. Robinson and Berz[7] have considered re-emission in an ionization gauge at low pressures, but their measurements were performed on the background gas whose composition was not known. The qualitative results of Hobson and Redhead[8] suggested that chemical pumping[6] of ionization gauges might play a significant role in ultra-high-vacuum systems, even in the absence of getters[9].

For these reasons the investigation presented in this paper of the pumping of nitrogen by a Bayard–Alpert gauge in an ultra-high-vacuum system was carried out concurrently with the measurements on physical adsorption[5]. The techniques, particularly the use of physical adsorption as an aid in analysis, and the general form of the results may be of interest for other quantitative work at very low pressures, since typical small ultra-high-vacuum systems were used.

2. Apparatus and general experimental procedure

The apparatus, which is shown in Fig. 1, has been described previously by the author[5], and details of its construction and processing will not be repeated here. The gas source was spectroscopically pure nitrogen. The main region of

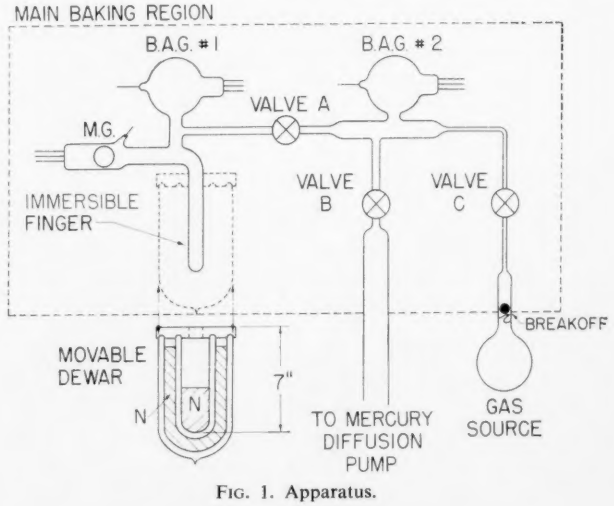

FIG. 1. Apparatus.

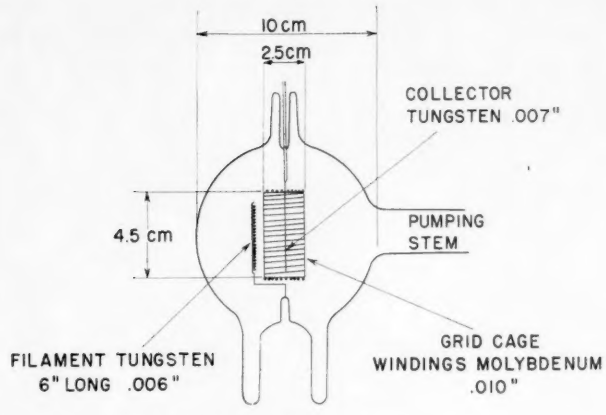

FIG. 2. Detail of Bayard–Alpert gauge.

interest was volume V (approximately 1 litre) to the left of valve *A*, and the Bayard–Alpert gauge[10] studied was BAG–1, whose details of construction are shown in Fig. 2. The magnetron gauge, shown as *MG* in Fig. 1, was not used in the present measurements. The operations central to the present experiments are now listed.

(a) The settings of all valves, in particular valve *A*, were continuously variable from fully closed to fully open.

(b) The finger could be immersed to a fixed mark in liquid nitrogen or removed from the liquid nitrogen at any time.

(c) The electron current I^- of *BAG*–1 was continuously variable from 8 milliamperes to zero by means of variable filament temperature. The d.c. voltages used were: collector, 0 V; grid, +300 V; filament, +45 V. At any filament temperature I^- could be reduced suddenly to zero by removing the filament d.c. connection and permitting this electrode to float.

The gauge ion current of *BAG*–1 was continuously measured with a Beckman micro-micro-ammeter, model *V*, and recorded on a Speedomax Type G recorder, the whole measuring system having a response time of about 1 sec. The observed ion currents were converted to pressure *P* by means of

$$P = \frac{KI^+}{I^-} \text{ mmHg} \qquad (1)$$

where I^+ is the measured ion current,
I^- is the electron current,
$K = 0.04$ mmHg.

This value of *K* was given by the manufacturer for gauges of this design and no absolute check of its validity was made in these experiments. (Observations have been made in this laboratory by Redhead and Kornelsen[11], and elsewhere by Carter and Leck[12], in which *K* was not always constant with varying I^-, but the experiments to be described provide certain internal checks on the validity of equation (1) and it appears to be satisfied throughout these experiments.)

Before any nitrogen was permitted to enter *V* a stable pressure $P \leqslant 10^{-10}$ mmHg was achieved therein, and all operations subsequently performed with nitrogen were performed on the background gases, whose main constituent was helium. The results given below are for nitrogen with the background subtracted. Thus we neglect as quantitatively unimportant exchange interactions of the type studied by Brown and Leck[13], and by Carmichael and Trendelburg[14]. A justification of this assumption may be made from the results of these workers and is given in the Appendix.

The degree of outgassing and previous history of the gauge influenced the magnitude but not the nature of the observations. Results are given for two cases.

(1) Before any exposure to nitrogen the gauge was outgassed for three hours at grid current 200 milliamperes d.c., grid-to-filament voltage 800 V a.c., with valves *A* and *B* open, and with *C* closed. During its first exposure to a dose of about 10^{17} nitrogen molecules this gauge is called a " clean gauge ".

(2) Following a dose of this size, outgassing the gauge under the above conditions for about one-half hour produced a reproducible gauge condition which was essentially independent of the number of prior exposures to doses of 10^{17} molecules. Such a gauge is called an " outgassed gauge ".

Measurements were made on three separate gauges with results in general agreement.

3. Objectives of the experiments

The differential equation expected to describe the variation of *P* in *V* is

$$\frac{dP}{dt} = -\frac{S_E}{V}P - \frac{S_C}{V}P - \frac{S_A}{V}P + R_E + R_C + R_A + R_v \qquad (2)$$

where V is the volume to the left of valve *A* (l.),
S_E is the electronic pumping speed (l/sec),
S_C is the chemical pumping speed (l/sec),
S_A is the adsorption pumping speed of the finger when immersed in liquid nitrogen (l/sec),
R_E is the rate of rise in the partial pressure corresponding to re-emission of molecules previously pumped electronically (mmHg/sec),
R_C is the rate of rise in the partial pressure corresponding to re-emission of molecules previously pumped chemically (mmHg/sec),
R_A is the rate of rise in the partial pressure corresponding to re-emission of molecules previously pumped by adsorption in the finger (mmHg/sec),
R_v is the rate of rise in the partial pressure corresponding to arrival of molecules through valve *A* (mm/sec). In all these experiments R_v was positive or zero.

Here we have followed the general procedure of Alpert[6] by dividing the pumping processes present in a gauge into those requiring an electron beam, which we term " electronic pumping ", and those which do not require an electron beam, which we term " chemical pumping ".

Equation (2) has the simplified form

$$\frac{dP}{dt} = -\frac{P}{\tau} + R \qquad (3)$$

where

$$\tau = \frac{V}{S_E + S_C + S_A} \qquad (4)$$

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and

$$R = R_E + R_C + R_A + R_v \quad (5)$$

where τ is the characteristic time representing all pumps present,

and R represents all sources present.

We will examine equation (3) in particular when $\tau = \tau_G = V/(S_E + S_C)$ and $R = R_E + R_C + R_v$; that is, when the physical adsorption pump is absent and the pumps present are characteristic of the Bayard–Alpert gauge, and possibly other parts of the system.

Provided R and τ_G are constant during a set of observations, equation (3) has the simple solution

$$P = P_\infty + (P_0 - P_\infty)\exp(-t/\tau_G) \quad (6)$$

where $P = P_0$ at $t = 0$, and

$$P_\infty = R\tau_G \text{ is the equilibrium value of } P \text{ as } t \to \infty. \quad (7)$$

The first experimental objective (Section 4(a)) was to measure τ_G and R independently and to establish the validity of equations (3), (6) and (7) for the system being used. Once the general validity of these equations was established, then the measurement of either R or τ_G by any method based on the equations was sufficient to determine the other since P was continuously observed. Sections 4(b), (c), (d), (e), (f) describe various experiments designed to separate S_E, S_C, R_E, and R_C, to measure their approximate magnitudes, and to isolate the main parameters on which they depended.

The major parameter upon which these four quantities depended was the number of nitrogen molecules N_p which had previously been pumped by the gauge. N_p was obtained from the relation

$$N_p = 3.3\times 10^{19}\, V \int_0^t \frac{P}{\tau_G}\,dt \quad (8)$$

(with V in litres and P in mmHg)

Since τ_G was slowly varying with time it was necessary to measure τ_G periodically to apply equation (8).

Alternatively, the number of molecules which had entered the system through valve A (N_v) could be obtained from

$$N_v = 3.3\times 10^{19}\, V \int_0^t R_v\,dt \quad (9)$$

where R_v is in mmHg/sec.

Clearly R_v must be known as a function of time for application of equation (9).

Neglecting molecules in the gas phase, N_p in principle exceeds N_v only by the molecules which are re-emitted and then repumped by the gauge. This number was found to be small for nitrogen and for most purposes equations (8) or (9) were used, as convenient. Formally equations (8) and (9) make no distinction between molecules pumped electronically and chemically, but the interpretation placed on the measurements of τ_G permits this in principle, although it has not been done in this paper.

4. Experiments and results

(a) *Establishment of the equations of the system*

Fig. 3 shows the result of an experiment with fixed R_v (that is, valve A set and the pressure measured on BAG–2 much greater than P and constant with time.) At zero time in Fig. 3, BAG–1, with $I^- = 80$ microamperes, was pumping against the input leak and a slowly rising value of $P = P_1$

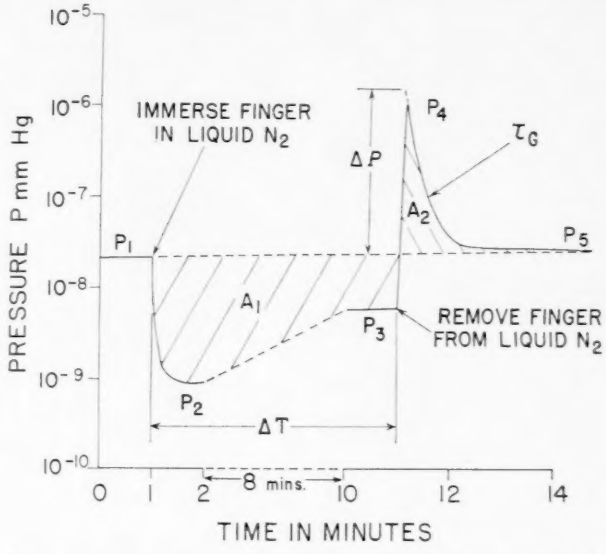

FIG. 3. Immersion experiment for measurement of τ_G and R ($I^- = 80$ microamperes).

was found. (The observed ion currents have been converted to pressure by means of equation (1).) After 1 min the finger was immersed in liquid nitrogen to a fixed mark, the area of Pyrex in contact with liquid being 60 cm². The pressure fell rapidly by a factor of about 50 to a minimum, P_2, and thereafter climbed slowly as the amount of nitrogen adsorbed in the finger built up. At 11 min ($\Delta T = 10$ min) the liquid nitrogen was removed and the pressure rose from P_3 to a peak P_4 as the adsorbed nitrogen was released. Thereafter the pressure fell to P_5 at a rate from which the characteristic pumping time τ_G (if greater than 5 sec) was obtained using equation (6). The deviations of the measured pump-down from an exact fit of equation (6) (after the region of the initial peak) were so small that they were not measurable. Pump-downs of this type usually did not exceed two orders of magnitude in pressure. From τ_G a value of R was obtained from equation (7) with $P_\infty = P_5$. R was also obtained independently by the method now described.

When the areas corresponding to A_1 and A_2 in Fig. 3 were measured from a linear plot of pressure (or current) versus time, they were equal within experimental error, demonstrating that all the nitrogen pumped by the finger during immersion was released upon desorption. Thus the peak pressure P_4 gave an approximate measure of the quantity of nitrogen trapped in the finger at the time of desorption. P_4 would have given an accurate measure of this amount if desorption and the response of the measuring system were infinitely fast. An estimate of this ideal result may be made by extrapolation of the observed pressure backward in time following equation (6) until a vertical rise-time gave the measured value of A_2. The value of ΔP thus obtained is considered accurate to ± 15 per cent provided $\tau_G \geqslant 5$ sec. To relate ΔP to R a correction to ΔP must be made for the

TABLE I

Experiment Number	I^- (μA)	Time after R_v established (hr)	P_∞ (mmHg)	τ_G (sec)	A_1 (coulombs)	A_2 (coulombs)	ΔT (sec)	ΔP (mmHg)	r	$\frac{\Delta P}{\Delta T(1-r)}$ (mmHg/sec)	$\frac{P_\infty}{\tau_G}$ (mmHg/sec)
1	80	6.25	2.6×10^{-8}	11	2.4×10^{-8}	2.5×10^{-8}	600	1.5×10^{-6}	0.13	2.8×10^{-9}	2.4×10^{-9}
2	80	8.5	6.0×10^{-8}	22.5	6.1×10^{-8}	5.7×10^{-8}	600	1.6×10^{-6}	0.06	2.8×10^{-9}	2.7×10^{-9}
3	80	20.75	5.9×10^{-8}	23	6.9×10^{-8}	6.8×10^{-8}	720	1.7×10^{-6}	0.06	2.5×10^{-9}	2.6×10^{-9}

quantity of gas pumped by the gauge during immersion. During an immersion the mean pressure at the gauge $(P_2 + P_3)/2$ was reduced below the mean pressure with the finger at room temperature by the factor

$$r = (P_2 + P_3)/(P_1 + P_5). \tag{10}$$

Thus during immersion the gauge pumped a fraction r and the finger a fraction $1 - r$ of the total input. P_1 and P_5 were not quite equal because τ_G was slowly varying during the immersion. Hence

$$R = \frac{\Delta P}{\Delta T(1 - r)}. \tag{11}$$

Analyses of three experiments of the type shown in Fig. 3 are given in Table I for a run on a clean gauge for which R_v was established and left constant for 50 hr. The values of R obtained by the two methods described above and shown in the last two columns of the Table are sensibly the same.

The two methods, however, are not fully independent since each depends upon a clear separation of the pump-down curve and any transient effects due to warming the finger. Empirically when $\tau_G \geqslant 5$ sec, consistent results were obtained. When $I^- = 8$ milliamperes, τ_G was always less than 5 sec, and values of R obtained by the above methods at 8 milliamperes were lower than those obtained at 80 microamperes, the discrepancy being a factor of three when $\tau_G = 1.5$ sec. However, equality of areas A_1 and A_2 was maintained at $I^- = 8$ milliamperes and relative heights of the desorption peaks at $I^- = 8$ milliamperes were useful.

Assuming that R remains nearly constant during the short time required to establish a new equilibrium pressure, P_2, when the finger is suddenly immersed in liquid nitrogen, then the adsorption pumping speed as measured by the gauge should be given by

$$S_A = \frac{V}{\tau_G}\left(\frac{P_1}{P_2} - 1\right) \tag{12}$$

where P_1 is the equilibrium pressure preceding immersion of the finger. It was found empirically for $R_v < 10^{-8}$ mmHg/sec that values S_A obtained from equation (12), with P_1 and P_2 as given in Fig. 3, were constant within a factor of two throughout these experiments, with a mean value of 3.5 l/sec. The calculated tubing conductance between the entry point of nitrogen and the cold portion of the finger was 3.8 l/sec, obtained by assuming 17 cm of tubing (i.d. 2.2 cm) at 295 °K, and 8 cm at 186 °K (mean between room and liquid nitrogen temperature). Thus the simple immersion of the finger was sufficient to yield an approximate value of V/τ_G, and hence of R. An important feature of these uses of the cold finger is that operating voltages of the gauge were not changed during the measurements.

From analyses of the data such as those presented in Table I it was concluded that at any fixed value of I^- equations (3), (6) and (7) were valid and that quantitative conclusions based on these equations after either R or τ_G had been measured were legitimate. For example, the result given in Table I, that R did not change sensibly during the period 6 to 21 hr after establishment of R_v was taken to mean that this value of R was maintained from the start of the run, and hence only the observed equilibrium pressure was required to give the pumping speed. Following the 21-hr point in this experiment, R was found to rise by a factor of 1.4. The increment in R was interpreted as the advent of a contribution from $(R_E + R_C)$ to R. This gave a method of measuring $(R_E + R_C)$. A more direct method is given in Section 4(c).

(b) *Measurements of* $S_E + S_C$

Fig. 4(a) shows $S_E + S_C$ (obtained from $S_E + S_C = V/\tau_G$) for the run of Table I as a function of the number of molecules that entered the gauge through valve A. The plateaus in the decline of the pumping speed seen in Fig. 4(a) occurred during two nights, with I^- steady at 8 milliamperes. Their cause is not known and they were not investigated further. Secondary evidence (Section 4(e)(1)) assigned the speeds of Fig. 4(a) mainly to the gauge rather than the system as a whole. Similar results for an outgassed gauge, where the assignment of the speed to the gauge is unambiguous are shown in Fig. 4(b). A major difficulty here was the assignment of numerical values to the horizontal axis since no

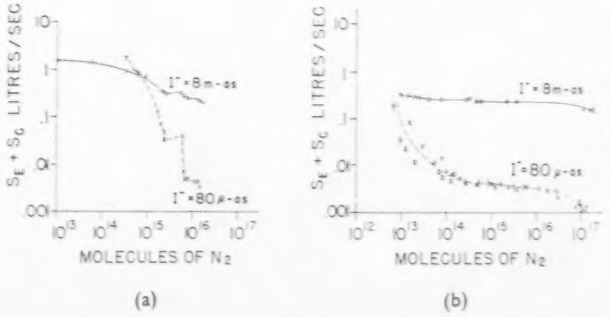

FIG. 4. Gauge pumping speed vs. number of molecules of nitrogen (a) supplied to clean gauge, (b) pumped by gauge after outgassing. Each symbol represents a separate run.

reliable criterion was available as a measure of gauge cleanliness. During outgas the whole gauge became warm and the pressure rose to an unknown value. Immediately after outgas the pressure fell quickly and after 10 min had reached a quasi-equilibrium value within factor of two of its final value, which was always higher than the equilibrium value achieved with a clean gauge. With $R_v = 0$, experiments on this background gas showed the same observable properties as experiments on nitrogen performed with $R_v \neq 0$. Hence this gas was assumed to be nitrogen and the counting of nitrogen molecules which determines the horizontal axis in Fig. 4(b) was arbitrarily commenced 10 min after outgassing ceased.

Despite these difficulties, which are further discussed in Section 5.1(b), Figs. 4(a) and 4(b) demonstrate that at small values of N_p (molecules pumped by the gauge) the pumping speeds at 8 milliamperes and 80 microamperes are comparable in magnitude and higher than is to be expected for electronic pumping alone. The cross-over of the pumping speeds shown in Fig. 4(a) will be discussed in Section 4(e)(1). As N_p increases, both speeds fall to values representative of electronic pumping alone at about $N_p = 10^{15}$ in Fig. 4(b). These values correspond satisfactorily with electronic pumping speeds for nitrogen summarized by Alpert[6]. The decline in speed near 10^{17} molecules may also be identified with the decline in electronic pumping speed studied by Bills and Carleton[2]. This suggests that the high values of speed found at low values of N_p be assigned primarily to a rise in S_C. However, before more direct experimental evidence for this identification is presented in Section 4(d), some results on $R_E + R_C$ will be described.

(c) *Measurements of* $R_E + R_C$

The most direct method of measuring $R_E + R_C$ was to close A (that is, $R_v = 0$) after a known number of molecules had entered and, with τ_G known, to measure the equilibrium pressure. Results obtained on outgassed gauges are shown in Fig. 5(a). Most measurements were made about an hour after completion of pumping, which took 2–4 hr for the cases shown. It is estimated that values of $R_E + R_C$ less than 5×10^8 molecules/sec were not distinguishable from background effects. From Fig. 5(a) the re-emission probability was 10^{-5} to 10^{-6}/sec/molecule pumped about an hour after completion of pumping. This result is applicable to R_E but it represents only an upper bound for R_C since re-emission after the chemical pump had declined was not distinguishable from the background. The re-emission was found to fall with time following completion of pumping. Fig. 5(b) shows a record of pressure against time, with $I^- = 8$ milliamperes and valve A closed, following the pumping of 1.5×10^{17} molecules. No change in speed was measured during this pump-down, which is shown in Fig. 5(a) by a vertical arrow. From Fig. 5(b) the time rate of fall of re-emission of nitrogen in a Bayard–Alpert gauge appears slower than for the inert gases in nickel and molybdenum where Carmichael and Knoll[15] found a t^{-1} dependence. The periodicity seen in Fig. 5(b) was real, and will be discussed in Section 4(e). The results of Section 4(f) also suggest that $R_E + R_C$ should depend somewhat on the value of I^-, but the conditions under which the data of Fig. 5(a) were taken were not sufficiently well controlled to demonstrate this dependence.

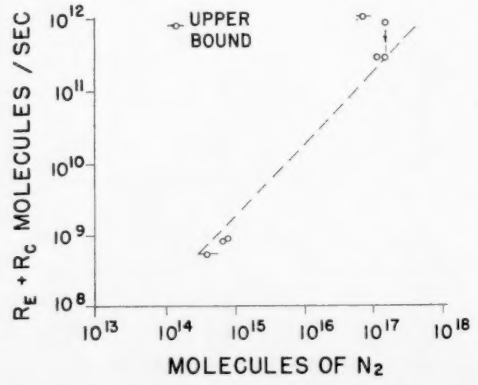

FIG. 5(a). Re-emission vs. number of molecules of nitrogen pumped by outgassed gauge. Each point represents a separate run.

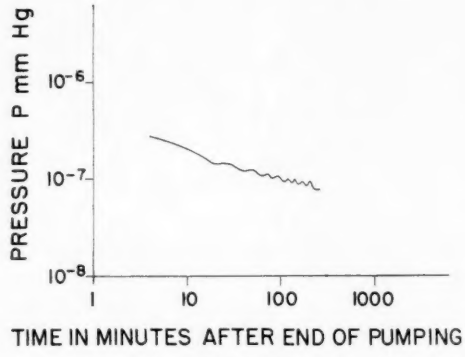

FIG. 5(b). Pressure vs. time after pumping 1.5×10^{17} molecules by outgassed gauge.

The standard outgas was found to reduce the re-emission by two to three orders of magnitude. Thus, after the pumping of about 10^{17} molecules, followed by a standard outgas, pressures between 10^{-9} and 10^{-10} mmHg were achieved at $I^- = 8$ milliamperes ; whereas with a clean gauge before the introduction of nitrogen, pressures $\leqslant 10^{-10}$ mmHg were achieved.

(d) *Separation of* S_E *and* S_C

Three types of measurements were made with a fixed external leak where R_v had been measured and $R_v \gg R_E + R_C$. In the first type, illustrated in Fig. 6(a), I^- was reduced suddenly from 8 milliamperes to zero by floating the filament. I^+ immediately fell to zero. I^- was restored suddenly to 8 milliamperes some time later ($\Delta T = 1$ min in Fig. 6(a)). I^+ rose to a peak and returned to the equilibrium value. The result of the experiment depended on the number of molecules the gauge had pumped (curves 1, 2, 3). The number of coulombs A_3 lost during ΔT (measured from a linear plot of I^+ against time) always exceeded the number A_4 gained when I^- was restored, but the ratio A_3/A_4 varied from a large value for N_p small, to a value approaching, but less than, unity for N_p large. The effect is so marked in curve 1 of Fig. 6(a) that A_3/A_4 is undefined. This area result

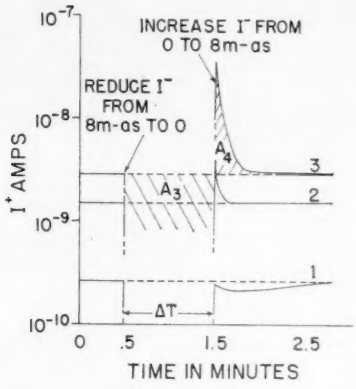

FIG. 6(a). Result of switching off I^- for a known time. Fixed input leak.

Curve 1 : Clean gauge $N_p = 5\times10^{13}$
Curve 2 : Clean gauge $N_p = 2\times10^{15}$
Curve 3 : Clean gauge $N_p = 1.5\times10^{16}$

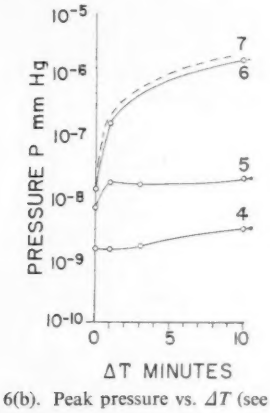

FIG. 6(b). Peak pressure vs. ΔT (see Fig. 6(a)).

Curve 4 : Clean gauge $N_p = 5\times10^{13}$
Curve 5 : Clean gauge $N_p = 2\times10^{15}$
Curve 6 : Clean gauge $N_p = 1.5\times10^{16}$
Curve 7 : Calculated pressure if all pumps zero when $I^- = 0$.

was interpreted as demonstrating that the molecules which would have been pumped electronically with $I^- = 8$ milliamperes were taken up chemically while $I^- = 0$; that is, S_C is separable from S_E. The reduction of A_3/A_4 then means a reduction of S_C/S_E with $S_C/S_E \to 0$ as $A_3/A_4 \to 1$.

This result was examined in a different way by plotting pressure obtained from the peaks in Fig. 6(a) versus ΔT. The results are shown in Fig. 6(b) in curves 4, 5, 6, which correspond respectively to curves 1, 2, 3 in Fig. 6(a). The dashed curve, 7, represents the expected pressure rise calculated from R_v under the assumption that all pumping speeds were reduced to zero when $I^- = 0$. Curve 7 is sensibly valid numerically for cases 4, 5, and 6. From these curves, values of S_C may be calculated conveniently from equations (3), (4) and (5), with $\tau = V/S_C$, $R = R_v$. The central conclusion is that the rise in $S_E + S_C$ at small values of N_p is caused by a rise in S_C, and that S_C may be dominant in a clean gauge.

(e) *Dependence of S_E and S_C on I^-*

A third type of experiment giving the same major conclusion, but supplying data on some other parameters upon

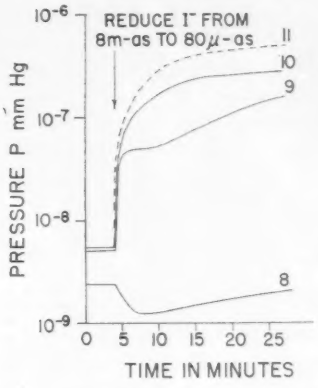

FIG. 6(c). Result of switching I^- from 8 milliamperes to 80 microamperes. Fixed input leak.

Curve 8 : Clean gauge $N_p = 3.5\times10^{14}$
Curve 9 : Outgassed gauge $N_p = 10^{14}$
Curve 10 : Outgassed gauge $N_p = 5\times10^{14}$
Curve 11 : Calculated pressure for curves 9 and 10 if all speeds proportional to I^-.

which S_E and S_C depend, is shown in Fig. 6(c). Here I^- was suddenly switched from 8 milliamperes to 80 microamperes, and pressure variations subsequent to this switch were monitored continuously by the gauge itself. Curve 11 shows the expected pressure rise for curves 9 and 10 calculated from R_v under the assumption that $S_C = 0$ and $S_E = BI^-$, where B is a constant. Two significant differences may be found upon comparing Figs. 6(b) and 6(c).

1. Curve 8, taken shortly after curve 4, shows a decisive pressure minimum (that is, increased pumping speed) which is reached about 4 min after the switch in I^-. The explanation proposed for the difference between 4 and 8 and also for minor dips in 1, 5, and 9, is that S_C depends on the temperature of portions of the gauge, this temperature being governed by the power input to the gauge. This power input was 22 W at $I^- = 8$ milliamperes, 20 W at $I^- = 0$ with filament floating but temperature unchanged, 10 W at $I^- = 80$ microamperes. These power changes were reflected in some measurements of the temperature of the outside of the bulb taken at a point an average distance from the filament. This temperature fell by 3 °C for a switch from $I^- = 8$ milliamperes to zero, and by 15 °C for the switch from $I^- = 8$ milliamperes to $I^- = 80$ microamperes, with a characteristic time of 3.5 min. A more detailed discussion of gauge temperature conditions is given in Section 5.1(b).

These results rule against the filament temperature itself being the decisive parameter, since filament temperature was directly reflected in I^- and these changes were complete within seconds. The dip in pressure following changes in power input became less emphasized as N_p increased, and at this stage results obtained with clean and outgassed gauges were not distinguishable ; hence they could be assigned decisively to the gauge rather than the system as a whole. At low values of N_p the dips for a clean gauge were even more marked and this suggests that the high values of S_C obtained with a clean gauge be assigned to the gauge rather than to other parts of the system.

2. A comparison of curves 6, 7, and 10, 11, shows closer

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agreement between 6 and 7 than between 10 and 11 where the discrepancy is nearly a factor of two. In both cases S_C was thought to be near zero. This suggested that even when $S_C = 0$ the assumption used in obtaining 11, namely $S_E = BI^-$ where B is constant, was not fully correct. The point is confirmed in Fig. 7, which gives a record of I^+ for fixed R_v ($R_v \gg R_E + R_C$) for values of I^- decreasing in steps. Under the conditions R_v fixed, $S_C = 0$, $S_E = BI^-$, the equilibrium values of I^+ should be independent of I^-, since from equation (1)

$$I^+ = I^-P/K = I^-R_V/S_EK = R_v/BK. \tag{13}$$

The equilibrium currents were re-established upon increasing I^- again in similar steps, demonstrating that these levels were functions of I^- rather than time. The equilibrium current for $S_C \neq 0$ should be given by

$$I^+ = \frac{R_v/K}{B + S_C/I^-}. \tag{14}$$

It is easily shown from (14) that for $S_C \neq 0$ the ratio of equilibrium currents at $I^- = 8$ milliamperes and 4 milliamperes should be less than the ratio of equilibrium currents at $I^- = 100$ microamperes and 50 microamperes. However, the inverse was found, indicating $S_C \cong 0$. Thus B appears to increase as I^- falls from 8 milliamperes to 50 microamperes. Detailed analyses of the variations of Fig. 7 support the

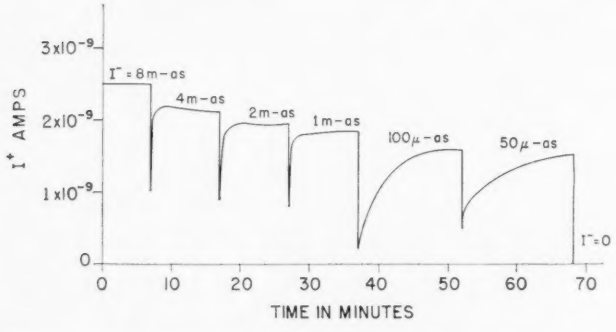

FIG. 7. Variation of I^+ with I^- for fixed input leak. Outgassed gauge $Np = 5 \times 10^{14}$.

conclusion that B rather than K in equation (1) is varying. One parameter upon which B might depend is the bulb temperature which varies in relative steps in the same way as the equilibrium currents in Fig. 7. Young[1] has shown that ionic pumping in a Bayard–Alpert gauge takes place mainly at the gauge walls, and Robinson and Berz[7] have shown by direct measurement that total gauge pumping speed does depend on the temperature of the bulb. However, attempts to make a detailed correlation between B and bulb temperature immediately following a switch to I^- were not successful. Redhead[16] suggests that B may depend on the potential of the glass walls which he has measured to change with I^-. Further experiments are required to clarify the details of the dependence of B on I^-.

(f) *Dependence of R_E on bulb temperature*

Fig. 8 gives the observed current against time following the change of I^- from 0 to 8 milliamperes in an experiment of the type shown in Fig. 6(a) with valve A closed (that is, $R_E \gg R_v$)

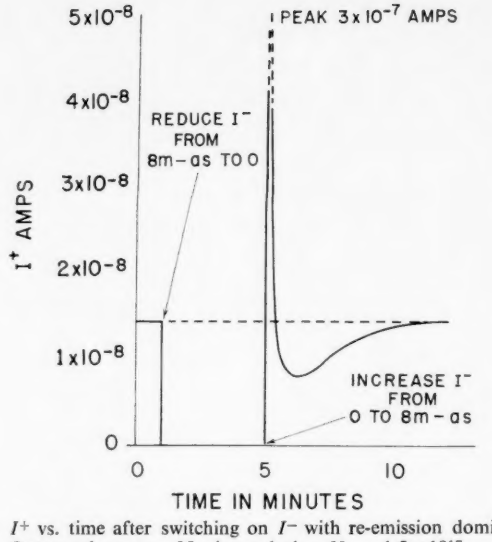

FIG. 8. I^+ vs. time after switching on I^- with re-emission dominant. Outgassed gauge. No input leak. $N_p = 1.5 \times 10^{17}$.

and the gauge pumping against the re-emission R_E from 1.5×10^{17} previously pumped molecules. The pronounced minimum 2 min after turn-on is not observed in Fig. 6(a) curve 3, which is characteristic of the case $R_v \gg R_E$ and hence is probably the result of variation in R_E. The time dependence is in agreement with that of bulb temperature. On this occasion also, 10 per cent variations of equilibrium current with the same frequency as variations of 2°F in room temperature were observed (the periodicity in Fig. 5(b)). Such a temperature dependence corresponds to an energy of adsorption of ionically pumped nitrogen of about 20 k-cal/mole. Leck[17] has measured the thermal desorption of gases, including nitrogen, previously pumped as ions into the walls of a Bayard–Alpert gauge, and reports a heat of adsorption similar to the above ; that is, intermediate between a heat typical of physical and chemical adsorption.

5. Discussion

The main findings are now listed and discussed.

1. In a clean or outgassed Bayard–Alpert gauge in an ultra-high-vacuum system, a chemical pumping speed for nitrogen was always found. This speed was of the order of 1 l/sec for a clean gauge, and of the order of 0.1 l/sec for an outgassed gauge. This pump had decayed after about 10^{15} molecules of nitrogen had been pumped. The speed of the pump was found to increase slowly (characteristic time, 4 min) when the filament temperature was reduced quickly (characteristic time, 1 sec) from 2100°K ($I^- = 8$ milliamperes) to 1800°K ($I^- = 80$ microamperes), the increase being at most a factor of two.

Several mechanisms will be examined as the possible source of this pump.

(a) The pump was present during the establishment of chemisorption equilibrium at the surface of the filament.

During outgas the filament was raised to a temperature near 2500°K and hence was cleaned. It was subsequently operated at 2100°K and 1800°K. At 1800°K nitrogen might be expected to have a sticking probability of 0.03

(Kisliuk[18]). With a filament area of 0.7 cm² the pumping speed would be about 0.2 l/sec. An extrapolation of Kisliuk's isotherms yields an equilibrium number of molecules adsorbed at 1800°K on our filament of 2.4×10^{10} at a measured pressure of 2×10^{-9} mmHg. Also, for this mechanism the pumping speed should follow filament temperature in time. Thus this mechanism is rejected as the cause of the main chemical pump. The mechanism was detected in our measurements in essentially the magnitude predicted by Kisliuk, from a rapid but short-lived pressure rise immediately following a switch from $I^- = 80$ microamperes to 8 milliamperes.

(b) Chemical pumping takes place on the other metal parts of the gauge ; that is, on the collector, grid, or filament supports.

During outgas the grid temperature was at least 1750°K and hence, from the results of Hagstrum[19], all adsorbed layers were removed. The other electrodes were at temperatures below this and hence their cleaning was probably not complete. However, during the equilibrating period between outgassing and measurement (about 10 min) the mean pressure was about 2×10^{-9} mmHg, and probably consisted of a mixture of gases produced when a Bayard–Alpert gauge is outgassed[20]. Under such conditions the major part of the first layer, in the sense of Becker and Hartman[4], should be complete on all tungsten and molybdenum surfaces, the degree of completion depending on the numerical value of the pressure during the equilibrating period. In a clean gauge this pressure might be expected to be less than in an outgassed gauge which has already pumped 10^{17} molecules of nitrogen. However, even if all of the first layer were complete we would not expect a major fraction of the second layer to be complete since the sticking probability for the second layer drops sharply. Thus at the start of measurements we might expect a pumping speed corresponding to a first layer which is just incomplete or just overcomplete, i.e. a pumping speed corresponding to the transition region between the first and second layer. The total area of the metal parts was about 20 cm² and a sticking probability of 10^{-2} would account for the initial pumping speed of the clean gauge, while a sticking probability of 10^{-3} would account for the initial pumping speed of the outgassed gauge. The results of Hagstrum[19] for nitrogen on molybdenum yield a sticking probability approaching unity for a sparse first layer, and 2×10^{-3} in the second layer. The transition between these values takes place mainly near the completion of the first layer. The mechanism suggested above gives reasonable agreement with these figures, if we postulate that a clean gauge gave a somewhat incomplete first layer at the start of measurements, while an outgassed gauge gave a complete first layer. Further, the capacity of the second layer for nitrogen on the metal parts should be about 2×10^{15} molecules. The results of Becker and Hartman[4] indicate a relatively strong temperature dependence of the sticking probability in the second layer for nitrogen on tungsten, in the temperature range in which the metal electrodes in a Bayard–Alpert gauge operate (e.g. at $I^- = 8$ milliamperes, the mean grid temperature due to electron bombardment is estimated at 650°K, and at $I^- = 80$ microamperes, at 360°K). Further, the temperature of these electrodes might be expected to change quite slowly following a change in power input to the gauge. Thermal loss by conduction begins to surpass loss by radiation for the grid near 600°K. The characteristic time for thermal cooling by conduction is given by

$$t = \frac{d^2 c \varrho}{k} \text{ sec} \tag{15}$$

where d is the specimen length,
c is the specific heat,
ϱ is the density,
and k is the thermal conductivity.

For both tungsten and molybdenum $t \approx 2.5\, d^2$. Since conduction paths lead out through the pinch we use a mean value of $d = 10$ cm, which yields a characteristic time near 4 min.

Thus we conclude that chemical pumping in the second layer on the metal parts of the gauge, particularly the grid, provides an acceptable explanation of the observed results. If this explanation is correct, then it follows that in ultra-high-vacuum systems metal parts which are not subjected to outgassing comparable to that of the grid of the Bayard–Alpert gauge are unlikely to show significant chemical pumping for nitrogen. Clearly, the results of our measurements are not sufficiently quantitative to establish the mechanism above as the only one present, and we examine two other possibilities.

(c) Evaporated metal films were responsible for chemical pumping.

During a standard outgas of one half-hour we estimate 1×10^{16} atoms of tungsten were evaporated from the filament, and 2×10^{16} atoms of molybdenum from the grid. This corresponds to about 1/10 monolayer of metal atoms on the walls of the gauge. No quantitative measurements appear to have been made on films of this concentration. Vacuum conditions similar to ours were used by Hickmott and Ehrlich[21] during some measurements on evaporated tungsten films. The objective of these workers was to evaluate under ultra-high-vacuum conditions previous work concerned with chemisorption on evaporated films. Hence they used evaporated amounts at least 100 times those estimated above. They concluded that any gas given off during evaporation was taken up by the film, but drew no quantitative conclusions concerning rates. Wagener[22, 23] has also measured the pumping speed of relatively thick films (approximately 1000 layers of metal) at very low pressures ($P \sim 10^{-8}$ mmHg). He found that clean tungsten and molybdenum films pumped nitrogen with a speed of 3 l/sec/cm². Wagener found that this speed was insensitive to the temperature of the film. The mean exterior bulb temperature in our experiments was about 320°K, and the interior temperature varied, at most, 20°K during the experiments described. The apparent temperature dependence of the observed chemical pump suggests that film pumping did not contribute greatly to chemical pumping.

(d) Chemical pumping requires the prior interaction of electrons, ions, or photons with the pumping surface.

Many results[24, 25] have shown that the bombardment of

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ions permanently alters surface conditions and hence might influence chemisorption. Such a possibility was briefly considered by Hobson and Redhead[26], but in view of (b) above, the coupling between electronic and chemical pumping appears more likely to be thermal.

During some measurements on the use of liquid helium for the achievement of very low pressures in ultra-high-vacuum systems, Hobson and Redhead[8] found evidence for a process (termed " process II ") which had the properties: (1) $P_\infty > R\tau_G$ (c.f. Eq. (7) of this paper) when R was measured from the increase in pressure per unit time when I^- was switched off ; (2) the pressure spike upon warming the finger after immersion in liquid helium for a certain time was much larger than the pressure spike obtained when I^- was switched on after the same period with I^- off. Similar properties were also found in the present investigation (compare Fig. 3 with Fig. 6(a) curves 1 and 2). Here they have been interpreted as characteristic of chemical pumping, and it seems likely that chemical pumps were also present in the earlier work. The presence of chemical pumping speeds of a few l/sec, together with an internal source of gas, can explain a major observation of the earlier work that the addition of a liquid helium pump with a speed near 5 l/sec sometimes produced a pressure drop as low as a factor of two. Since the gas in question was physically adsorbed at liquid helium rather than liquid nitrogen temperature, it is probable that it was hydrogen. Hydrogen was subsequently found to be present in significants amounts in similar ultra-high-vacuum systems by Kornelsen[27]. The mechanism of chemical pumping of hydrogen, however, is not necessarily the same as for nitrogen.

2. The re-emission probability of nitrogen molecules pumped chemically in a Bayard–Alpert gauge was less than 10^{-6}/sec/molecule under normal gauge operating conditions.

3. The electronic pumping speed for nitrogen in a Bayard–Alpert gauge was about 0.25 l/sec at $I^- = 8$ milliamperes until about 10^{17} molecules had been pumped, when a decline took place. This result is in agreement with the results of Bills and Carleton[2], and in partial disagreement with the results of Young[1] who found a decline after 2×10^{14} molecules had been pumped.

4. The re-emission probability of electronically pumped nitrogen was found to be 10^{-5} to 10^{-6}/molecule/sec, about one hour after pumping. Thus we consider that Bills and Carleton[2] were justified in neglecting re-emission in their calculations. This figure for nitrogen is similar in magnitude to the re-emission probabilities found by Carmichael and Knoll[15] for the noble gases on nickel and molybdenum about one hour after pumping.

Acknowledgements

The author wishes to acknowledge valuable discussions with P. A. Redhead and E. V. Kornelsen, and to thank all members of the Electron Physics Group for many and varied contributions to this work.

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APPENDIX

Gas Exchange

We estimate that after 10 days of normal operation, which was the longest run performed, and 5 hr of outgassing, 3×10^{14} atoms of helium had entered the system by diffusion from the atmosphere[28], and we assume all these were pumped ionically. Valves *A* and *B* were open during outgassing and hence this figure is an upper bound. Brown and Leck[13] give results for nitrogen bombarding ionically pumped helium with higher energies and greater amounts than those we are considering here, whereas Carmichael and Trendelenburg[14] give results for krypton bombarding ionically pumped helium under approximately the conditions we are considering, although in all cases the results were for metals. The two sets of results are in reasonable numerical agreement and we use the results of Carmichael and Trendelenburg. From their Fig. 10, the first pulse of 5×10^{16} ions of krypton released 3×10^{13} atoms of helium from nickel when 3×10^{14} ions of helium had previously been pumped. Thus one krypton ion released 6×10^{-4} atoms of helium. A typical bombarding flux of nitrogen ions in our experiments was 7×10^{10} per sec. Assuming that one nitrogen ion releases 6×10^{-4} atoms of helium we get an additional helium flux due to ion-induced re-emission of 4×10^{7} atoms/sec. The helium flux due to diffusion through Pyrex was about 10^{8} atoms/sec. Thus the additional input of helium remains smaller than the diffusion input even at the end of a run, and under these conditions ion-induced re-emission will not affect the results described above.

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The Sorption of Hydrogen by Barium Getters

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Sorption of hydrogen by barium films is shown to be made up of surface adsorption of the gas followed by its diffusion to the interior. The velocity of surface adsorption is studied at low pressures and its dependence on surface area, pressure and temperature is considered. The velocity of diffusion is examined for pressures and film thicknesses which are near to those in current industrial use. In this case too, particular attention is paid to the influence of temperature, as well as to the influence of parameters such as temperature of condensing walls, residual pressure at evaporation and time of flashing of the getter, all of which are of considerable practical interest.

Introduction

In a recent communication[1], data concerning the sorption of hydrogen by barium films were presented. These data made it possible to furnish a model of the sorption analogous to that previously described for nitrogen and carbon monoxide[2, 3, 4].

Through a kinetic study of the sorption it was in fact possible to distinguish a surface adsorption phenomenon from one of diffusion to the interior of the getter film, due to the differences in shape of the velocity of sorption curves depending on the pressure and temperature region investigated. These differences in behaviour are due to the fact that the overall phenomenon (made up of surface adsorption of the gas and of its subsequent diffusion to free barium atoms) proceeds with the velocity of the slowest one.

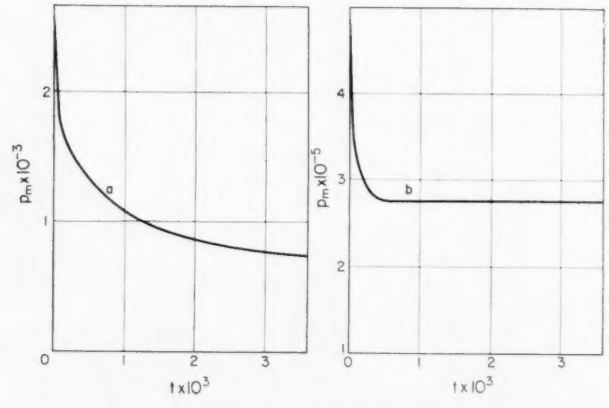

FIG. 1. Velocity of sorption for H_2 as a function of time at two different pressures.

t = time in sec
p_m = manifold pressure in Torr

Apparent surface area of film	100 cm²
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Temperature of sorption	298 °K
Constant pressure on getter	(a) 2.5×10^{-4} Torr
	(b) 3.7×10^{-6} Torr

In fact if the pressure is sufficiently high and the temperature sufficiently low, so that the hydrogen molecules which are adsorbed on the surface are in excess of those which can diffuse to the interior, then the latter will control the sorption velocity. On the other hand if the pressure is sufficiently low and the temperature sufficiently high so that the molecules sorbed on the surface may quickly diffuse towards the interior, the sorption velocity will depend only on the velocity with which fresh molecules can be adsorbed.

Typical results for these different conditions of sorption are shown in Fig. 1.

Curve (a) is distinctly decreasing with time, this is typical of a diffusion process, whilst curve (b) describes the behaviour of the velocity of surface adsorption. In both cases the sorption velocity was measured by keeping constant the chosen hydrogen pressure on the getter.

This point having been elucidated, in the present work the previously published results will be integrated and completed according to the following scheme :

1. Study the velocity of surface adsorption under those conditions which make it constant, that is to say on the basis of curves of type (b) in Fig. 1.
2. Study the diffusion phenomenon (curve (a)) of Fig. 1, on films whose thickness is of practical interest, to control if the results precedently obtained for thinner films are also applicable in this case.
3. Study the influence on diffusion (which is of prominent practical interest) of parameters of industrial importance, such as film thickness, temperature of condensing walls, residual pressure at evaporation and time of flashing of the getter.

Experimental

The apparatus employed in the present experiments is shown in Fig. 2.

The method of measurement is that described in a number of previous communications. It is based on the evaluation of the flow of gas, under Knudsen conditions, through a

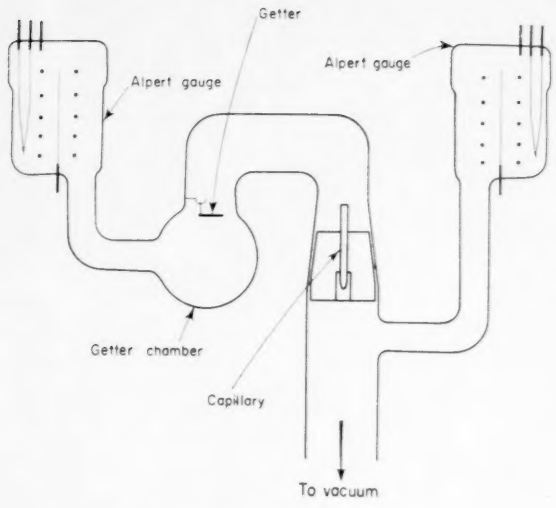

FIG. 2. Sorption apparatus.

capillary of known conductance. The dimensions of the capillary used in the present experiments are length 9.5 cm and diameter 2.02 mm.

All experiments were carried out at a constant pressure over the getter deposit. The film was evaporated from a stabilized barium-aluminium alloy getter ($St_2/7 \times 7$) which is capable of liberating 2 mg of barium. Getters of different types were only used when greater quantities of barium had to be evaporated, such as when studying the influence of surface area and thickness of the barium film.

Hydrogen pressure measurements with an ionization gauge are rather misleading due to the appreciable pumping by the gauge. It is well known that a tungsten filament[5] can bring about the dissociation of hydrogen molecules and that the atomic hydrogen thus formed is easily sorbed on the enclosing walls. The ionizing electron current also produces an appreciable effect[6, 7]. Nevertheless, by using very low electron ionizing currents the magnitude of the chemical pumping by the electron current may be kept to very low values. In fact all measurements previously carried out and those which will now be considered were obtained using an electron ionizing current of 0.01 mA ; the temperature of the filament under such conditions never rose above 1500 °K.

The measurements at various temperatures were carried out by employing suitable thermostatic baths. The hydrogen employed was supplied by British Oxygen Gases Ltd., London, and its impurity content was less than 2 p.p.m.

Results and discussion

Surface adsorption velocity

If the behaviour shown in curve (b) of Fig. 1 is closely analyzed, the existence of a small initial decrease in velocity is observed. This is followed, Fig. 3, by a stabilization to a constant velocity value. The quantity of gas adsorbed during this initial decreasing region is of the order of 10^{16} molecules. This may probably be related to the formation of an initial hydride layer.

The hydrogen molecules sorbed in such a manner are

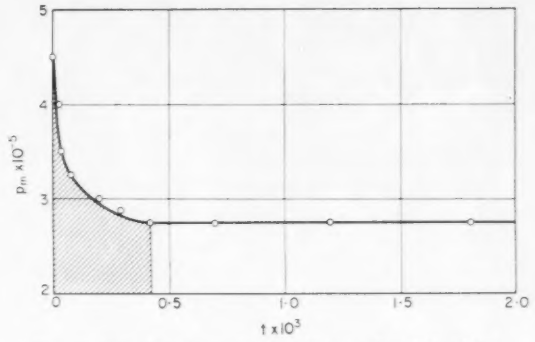

FIG. 3. Velocity of sorption for H_2 as a function of time.

t = time in sec
p_m = manifold pressure in Torr

Apparent surface area of film	100 cm²
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Temperature of sorption	298 °K
Constant pressure on getter	3.7×10^{-6} Torr

evidently not very mobile, and in all probability the initial decrease in velocity shows the dependence of the initial chemisorption on the degree of coverage of the metal surface exposed to the gas. One can deduce that a really constant velocity can only be achieved when a first layer has been almost completely formed. If one accepts such an hypothesis the constant velocity should be referred to the adsorption not on the metal but on the hydride already formed.

An accurate investigation of the initial decreasing region must be carried out at much lower pressures.

Nevertheless it is quite clear that the surface adsorption velocity which is effectively important in gettering is that of adsorption on the product of reaction already formed. Therefore, all the data presented in this section will refer to the velocity of surface adsorption which will be determined from the value corresponding to the horizontal region of the curve rather than from the initial value.

The velocity of surface adsorption as a function of the apparent area of the barium film is shown in Fig. 4. The

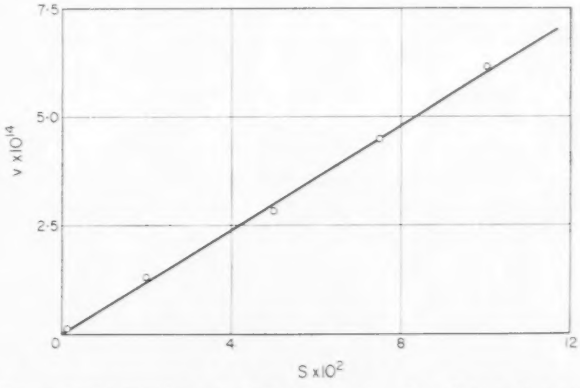

FIG. 4. Initial sorption velocity for H_2 as a function of the surface area of the barium film.

v = velocity in molecules sec^{-1}
S = surface area in cm^2

Weight of evaporated barium per cm²	0.02 mg
Temperature of walls at flashing	298 °K
Temperature of sorption	298 °K
Constant pressure on getter	1×10^{-5} Torr

measurements were carried out at a pressure of 1×10^{-5} Torr at room temperature. The quantities of evaporated barium were made to vary in such a manner as to maintain a nearly constant film thickness of 2×10^{-5} g cm^{-2}.

Since, as is to be expected, the velocity of adsorption is found to be directly proportional to surface area, it may be referred to unit area. At the pressure considered, 1×10^{-5} Torr, the velocity of surface adsorption is 6×10^{11} molecules sec^{-1} cm^{-2}.

The velocity of surface adsorption as a function of pressure is shown in Fig. 5. The measurements were carried out at

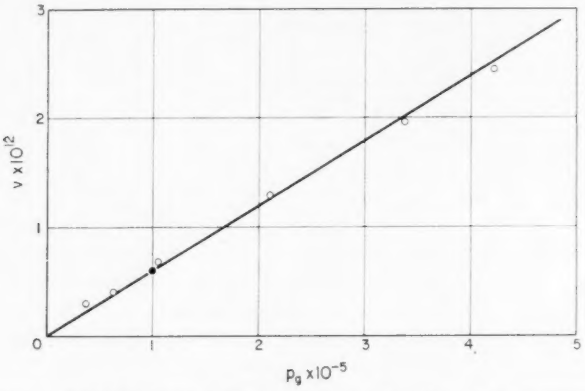

FIG. 5. Initial sorption velocity for H_2 as a function of the pressure on the getter film.

v = velocity in molecules sec^{-1}
p_g = constant pressure on getter in Torr

Apparent surface area of film	100 cm^2
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Temperature of sorption	298 °K

room temperature on a film of 2 mg which had an apparent surface area of 100 cm^2. The solid circle indicates the velocity referred to unit area, as calculated from Fig. 4. Since the velocity of surface adsorption is found to be directly proportional to the pressure, the mechanism appears to be one of molecular adsorption. Although the hydrogen molecules sorbed may subsequently dissociate into atoms, this does not seem to be the rate determining process.

Since the adsorption velocity is directly proportional to the pressure, all measurements may be referred to constant pressure. Thus the velocity becomes 6×10^{16} molecules sec^{-1}cm^{-2} Torr^{-1}.

Bearing in mind the fact that the number of hydrogen molecules which strike unit area of the barium film in unit time at room temperature is 1.99×10^{21} molecules sec^{-1}-cm^{-2} Torr^{-1}, the sticking probability is : $s = 4.17 \times 10^{-5}$.

This value appears rather low ; it is nevertheless of the same order of magnitude of that previously published by Perdjik[8] who finds $s = 11.25 \times 10^{-5}$ at room temperature. A comparison with the values published by Wagener is rather more difficult as they vary between about 1×10^{-3} [9,10] and 2×10^{-6}.[11]

The influence of temperature on the velocity of surface adsorption is shown in Figs. 6 and 7.

The curve in Fig. 6 was obtained with a film of 2 mg having an apparent surface area of 100 cm^2 and with a

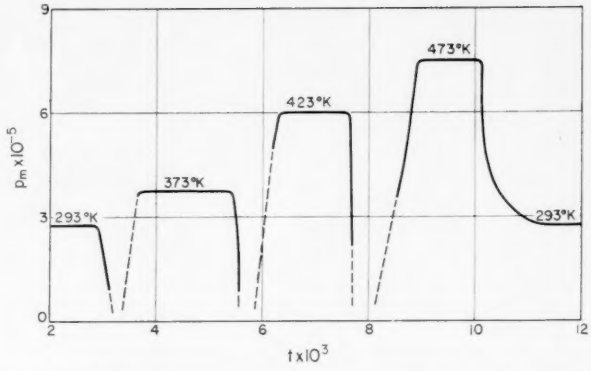

FIG. 6. Velocity of sorption for H_2 as a function of time at different increasing temperatures of sorption.

t = time in sec
p_m = manifold pressure in Torr

Apparent surface area of film	100 cm^2
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Constant pressure on getter	3.7×10^{-6} Torr

constant pressure of 3.7×10^{-6} Torr above the getter. The temperature of the getter was varied by a thermostatic bath in which the sorption vessel was immersed.

The first horizontal region of the curve corresponds to the velocity of surface adsorption for hydrogen at a temperature of 293 °K. After the consistency of this velocity had been ascertained for a sufficiently long period of time the temperature was increased to 373 °K. Initially, whilst the temperature was increasing, the velocity apparently decreased, in all probability due to the release of gas. This indicates that an appreciable quantity of hydrogen is lightly held on the surface. However, after a given time, the velocity increased once again to a value above the original one and then remained constant. The same behaviour was subsequently found during the process of increasing the temperature to 423 and 473 °K. At all these temperatures a constant velocity of surface adsorption was attained. This is shown by the various horizontal tracts of the diagram.

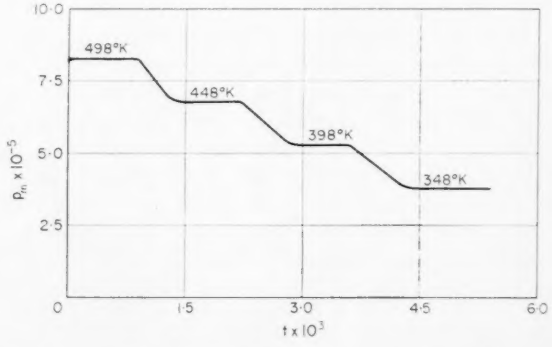

FIG. 7. Velocity of sorption for H_2 as a function of time at different decreasing temperatures of sorption.

t = time in sec
p_m = manifold pressure in Torr

Apparent surface area of film	100 cm^2
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Constant pressure on getter	3.7×10^{-6} Torr

Furthermore if the temperature is slowly decreased back to 293°K the velocity also falls to its original value, which confirms its constant value at a given temperature.

The curve in Fig. 7 was obtained under similar conditions to the above but the temperature was made to decrease from its highest to its lowest value. The previously observed degassing does not occur in this case and a stepwise decrease in the curve is obtained, each step corresponding to a constant velocity of surface adsorption at the given temperature.

From the sorption velocity values given in Figs. 6 and 7, it is possible to calculate the energy of activation for the process from the slope of the curve in Fig. 8 relating the

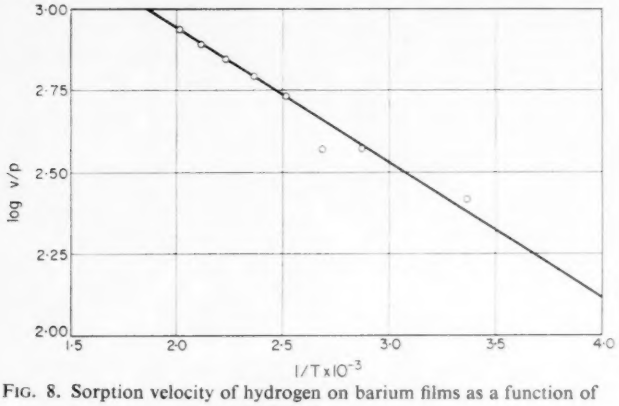

FIG. 8. Sorption velocity of hydrogen on barium films as a function of temperature.

v = velocity in molecules sec^{-1}
p = constant pressure on getter in Torr
T = sorption temperature in °K

Apparent surface area of film	100 cm^2
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298°K
Constant pressure on getter	3.7 × 10^{-6} Torr

logarithm of the sorption velocity to the reciprocal of the absolute temperature. This is found to be 1880 cal mole^{-1}. This value is slightly higher than that previously found, 1500 cal mole^{-1},[1] which was calculated from the initial velocity of sorption curves obtained at higher pressures and of the type shown in Fig. 1(a).

From the comments made in the introduction the present result should be considered as the more accurate.

Diffusion velocity

As pointed out in the introduction, this section is essentially concerned with the verification of the applicability of our previous results to thicknesses and pressure conditions comparable to those used in industry. Hence the results in this section refer to barium films of 2 mg having an apparent surface area of 15 cm^2, and the velocity of sorption was measured from curves of the type shown in Fig. 1(a).

The influence of temperature on diffusion is shown in Fig. 9, which gives the velocity of sorption at various temperatures as a function of time.

By graphical integration it is possible from such curves to evaluate the quantities of hydrogen sorbed at various given times, $Q_t = \int_0^t V(t)\,dt$, and by plotting these quantities against the square root of the corresponding times to obtain curves such as shown in Fig. 10. These curves present, after

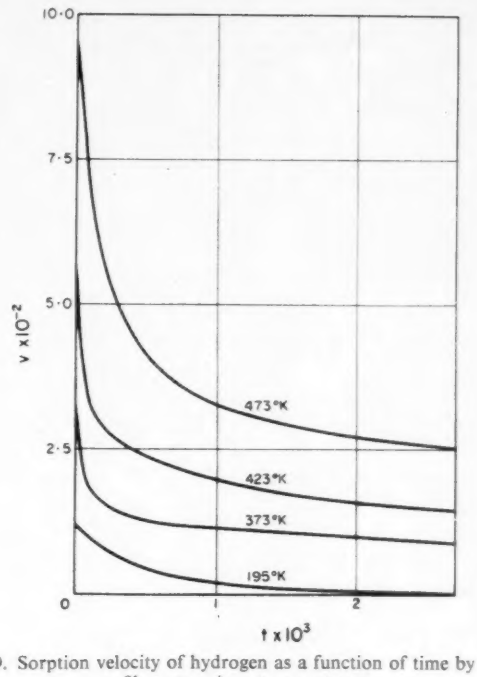

FIG. 9. Sorption velocity of hydrogen as a function of time by barium films at various temperatures.

v = velocity in cm^3 Torr sec^{-1}
t = time in sec

Apparent surface area of film	15 cm^2
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298°K
Constant pressure on getter	2.5 × 10^{-4} Torr

the initial region, an almost linear portion. It is well known that such linearity characterizes the quantity of gas which diffuses through a surface, on which the concentration of gas remains constant, when diffusion is assumed to occur in a semi-infinite medium.

At constant pressure and with this approximation the slopes of the straight lines (dQ_t/dt) are, through the diffusion coefficient, a function of temperature. It is therefore possible to evaluate the energy of activation for the diffusion process by considering the dependence of $D = D_0 e^{-\frac{E}{RT}}$ on temperature.

The logarithms of dQ_t/dt as a function of temperature are plotted in Fig. 11. The solid circles are the values as obtained from Fig. 10, whilst the open circles are the results previously published[1] for thinner films (2 mg/100 cm^2).

By comparing the two sets of points one draws confirming evidence for the hypothesis put forward concerning the kinetics of sorption, and in particular for the unique nature of the process even for getter films of very different thicknesses. The activation energy has a value of about 3000 cal mole^{-1}.

A discussion concerning the consequences of such a low potential barrier against diffusion of hydrogen towards the interior of the film has been previously put forward[1].

Parameters of industrial consequence and their influence on gettering

The velocity of sorption is shown as a function of the barium film thickness in Fig. 12.

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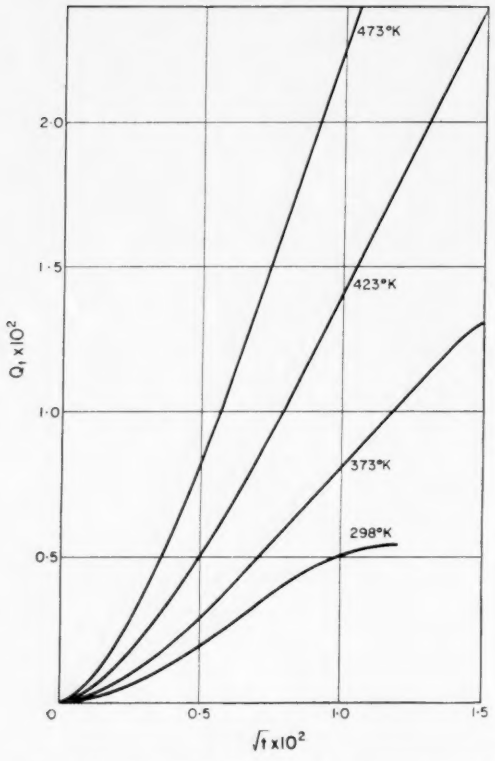

FIG. 10. Time dependence of the quantity of hydrogen sorbed by barium films at various temperatures.

t = time in sec
Q_t = quantity sorbed in cm³ Torr

Apparent surface area of film	15 cm²
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Constant pressure on getter	2.5×10^{-4} Torr

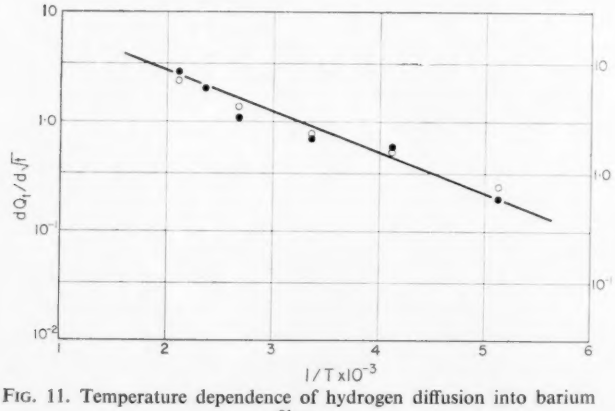

FIG. 11. Temperature dependence of hydrogen diffusion into barium films.

Q_t = quantity sorbed in cm³ Torr
t = time in sec
T = sorption temperature in °K

Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Constant pressure on getter	2.5×10^{-4} Torr

It illustrates how the velocity of diffusion (not only the capacity) increases with film thickness. Bearing in mind the granular structure of the film this result may be attributed to the different surface areas from which diffusion originates.

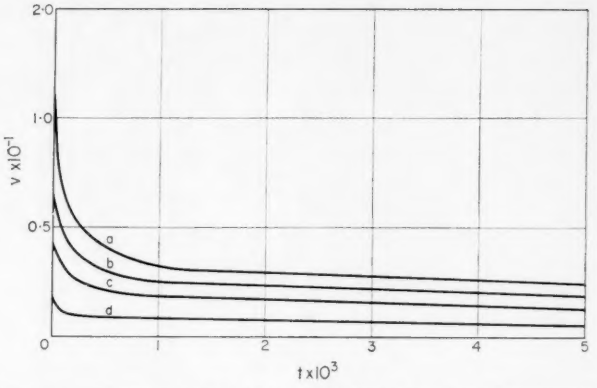

FIG. 12. Sorption velocity for H_2, for different quantities of evaporated barium, as a function of time.

v = velocity in cm³ Torr sec⁻¹
t = time in sec

Apparent surface area of film	15 cm²
Temperature of walls at flashing	298 °K
Temperature of sorption	298 °K
Constant pressure on getter	2.5×10^{-4} Torr
Weight of evaporated barium	(a) 18.7 mg
	(b) 13.8 mg
	(c) 8.3 mg
	(d) 2.0 mg

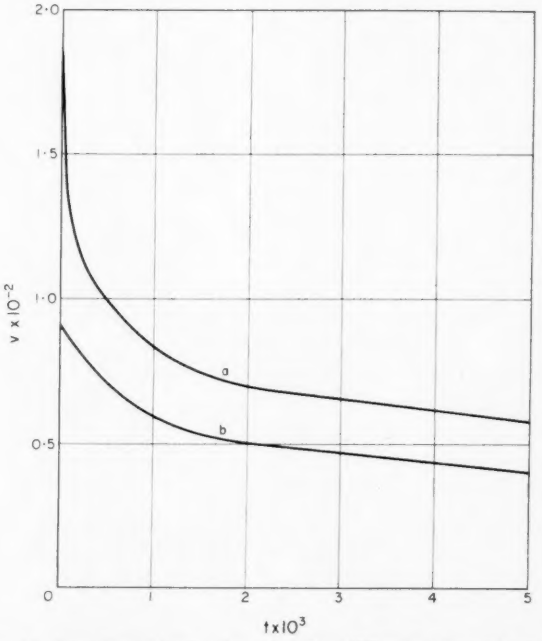

FIG. 13. Sorption velocity for H_2, for different temperatures of condensing walls, as a function of time.

v = velocity in cm³ Torr sec⁻¹
t = time in sec

Apparent surface area of film	15 cm²
Weight of evaporated barium	2 mg
Temperature of sorption	298 °K
Constant pressure on getter	2.5×10^{-4} Torr
Temperature of walls at flashing	(a) 293 °K
	(b) 473 °K

This could imply an extremely rapid surface diffusion such as to guarantee a high degree of coverage of the real total surface area of the getter film.

It would seem to be an advantage, therefore, for hydrogen

sorption, to employ a film of an appreciable thickness, contrary to what had been previously found for other gases.

Similar observations may also be made on the influence of other factors which are able to affect the structure of the film.

Thus the influence of the temperature of the condensing walls on the velocity of diffusion is shown in Fig. 13. A decrease of the velocity of sorption may be produced by increasing the substrate temperature during film condensation, so decreasing the real total surface area of the film (formation of larger crystals and sintering of the film). The curves referred to above were obtained at room temperature and at a pressure of 2.5×10^{-4} Torr on 15 cm^2 getter films.

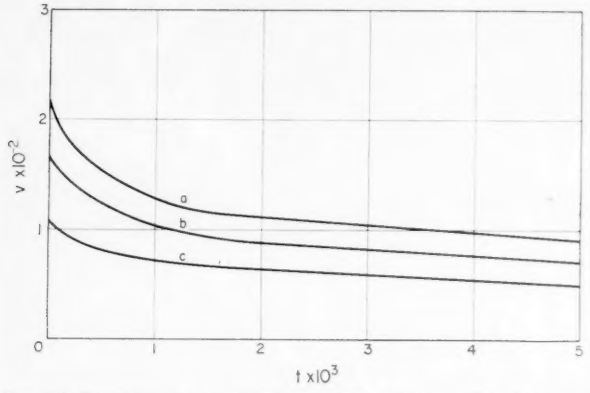

FIG. 14. Sorption velocity for H_2, for different times of flashing, as a function of time.

v = velocity in cm^3 Torr sec^{-1}
t = time in sec

Apparent surface area of film	15 cm^2
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Temperature of sorption	298 °K
Constant pressure over getter	2.5×10^{-4} Torr
Time of flashing	(a) 5 sec
	(b) 12 sec
	(c) 30 sec

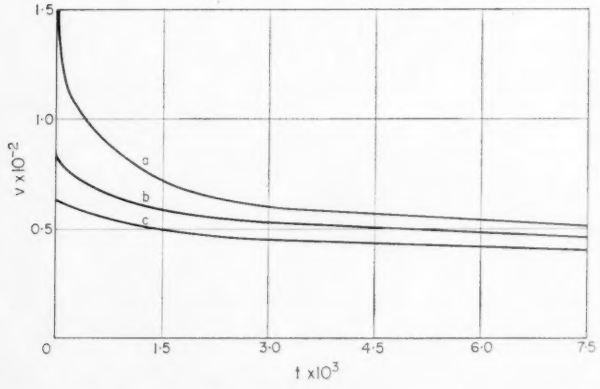

FIG. 15. Sorption velocity for H_2, for different residual pressures at flashing, as a function of time.

v = velocity in cm^3 Torr sec^{-1}
t = time in sec

Apparent surface area	15 cm^2
Weight of evaporated barium	2 mg
Temperature of walls at flashing	298 °K
Temperature of sorption	298 °K
Constant pressure over getter	2.5×10^{-4} Torr
Residual pressure during flashing	(a) 1×10^{-5} Torr
	(b) 1×10^{-4} Torr
	(c) 2×10^{-3} Torr

The curves in Fig. 14 were produced under the same conditions as those in Fig. 13 except the substrate was held at room temperature during evaporation and the evaporation rate was varied. In this case the effect produced arises from the difference in the internal surface area of the films obtained using different times of evaporation.

Finally the influence of the residual pressure during barium evaporation is shown in Fig. 15. These curves too were obtained on films of 2 mg, having an apparent surface area of 15 cm^2, at room temperature and at a constant pressure over the getter of 2.5×10^{-4} Torr

It appears that the influence of the residual pressure is primarily due to a preliminary poisoning of the getter, in the same manner as had been previously found for nitrogen and carbon monoxide.

Conclusions

The velocity of surface adsorption and the velocity of diffusion within a barium film have been studied independently.

With reference to surface adsorption it has been possible to show two distinct phases, in the first of which the velocity decreases whilst in the second it remains constant.

Since the first phase corresponds to the adsorption of a quantity of gas comparable to that required for the formation of a monolayer, it has been deduced that the constant velocity of surface adsorption characterizes the adsorption of gas on the reaction product already formed. This is in agreement with the relatively high mobility of the adsorbed phase which would be inexplicable if one assumed direct chemisorption on the metal ; it also justifies the partial degassing occurring when increasing the temperature of the film.

Concerning the diffusion to the interior of the film, the picture previously put forward for thinner films has been verified for films of greater thickness.

Finally all the measurements carried out to study the influence of various parameters on the efficiency of gettering have contributed to show the importance of a barium film of high porosity.

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Letters to the Editor

Markings on Copper Electrodes after Electrical Breakdown in Vacuum

SEVERAL investigators[1–7] have mentioned the appearance of electrodes after many electrical breakdowns in vacuum. In general the anode contained large craters surrounded by a lip, which appeared to represent a melted surface, and the cathode had deposited on it solidified droplets of metal. Work by Maitland[8], using 4.5μsec pulses, has shown that the breakdown markings, occurring on copper anodes, were in his case made up of shallow craters 10^{-5}–10^{-4} cm diameter which covered the whole area of the mark, deep craters 10^{-4}–10^{-3} cm diameter which were shown to arise at impurity centres and on crystal boundaries; and eroded crystal edges. Pfeil[9] had previously shown that arcing occurred around inclusions in the cathode of a low pressure hydrogen discharge.

Using a direct voltage source, in which the breakdown current was limited by a 2 MΩ resistor, similar effects both in nature and size and further effects have been noted. The results were obtained from the electrodes of an apparatus, designed to test the clump theory[10], arranged so that a metallic surface could be examined with a voltage applied[11]. The cathode was in the form of a 3 cm diameter copper disc, while the copper anodes were made of 0.6 cm diameter drawn and annealed copper bar containing normal commercial impurities. The surface before each test was roughly mechanically polished on 600 emery cloth and then polished with metal polish to remove traces of the previous test. The pressure was 10^{-5}–10^{-4} Torr and the gap range 0.0375–0.075 cm.

The deep craters that were observed are shown in Fig. 1, the diameters being between 3×10^{-4} and 2×10^{-3} cm. It will be seen that the background appears to have been slightly etched. When gross breakdown markings occurred, of size 6×10^{-2}–10^{-1} cm diameter for gaps of 0.0375–0.05 cm, which are probably due to a longer time discharge, a striking preferential etching effect was observed, as seen in Figs. 2 and 3. In the case shown the gap was 0.05 cm, the breakdown voltage about 35 kV and the corresponding current about 18 mA. The time of the discharge was unknown. It will be seen that the action of the arc has been to etch out the surface, attacking some crystals and not others, leaving crystal islands. The actual straight line tracks appear to be made up of craters 10^{-4} cm diameter which are similar in size to the shallow craters previously reported. Maitland has postulated that such craters are formed simultaneously due to the ablation of material by a multi-beam stream of electrons which occurs during the first stage of breakdown and lasts, in the case of 4.5μsec pulses, for 10^{-8}–10^{-10} sec. Fig. 3 would seem to show that the formation of craters and the action of preferential erosion at the crystal boundaries and impurity centres is in fact continued throughout the length of the direct current discharge. Fig. 4

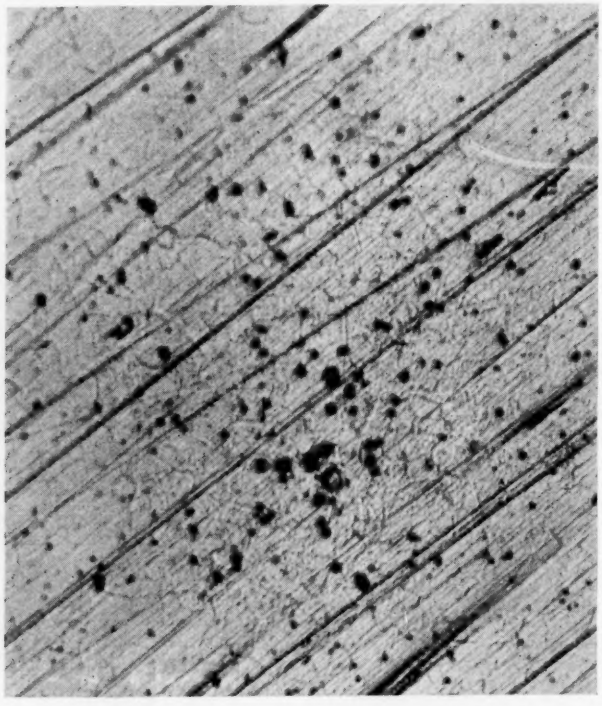

FIG. 1. Deep craters on copper anode surface. × 270.

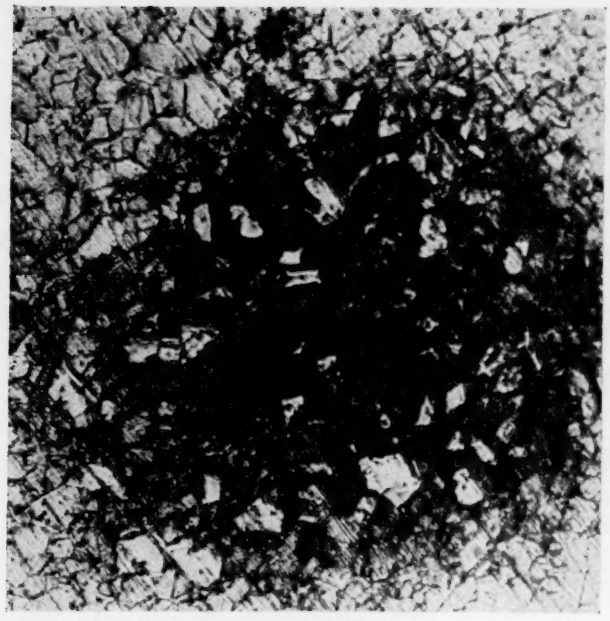

FIG. 2. Copper anode surface showing preferential etching in gross breakdown mark. × 180.

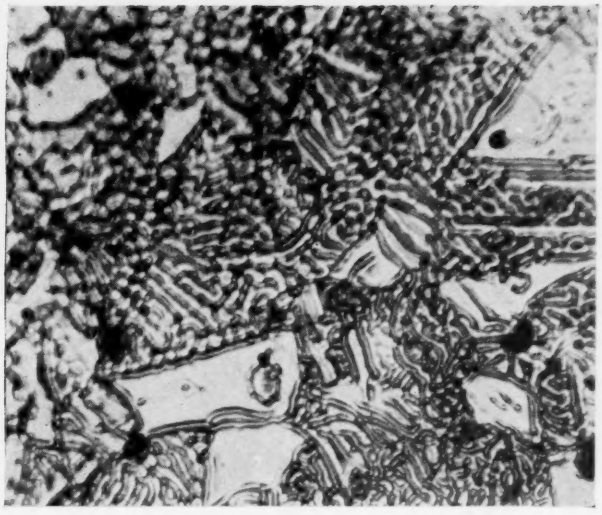

FIG. 3. As Fig. 2. Showing crystal islands. × 560.

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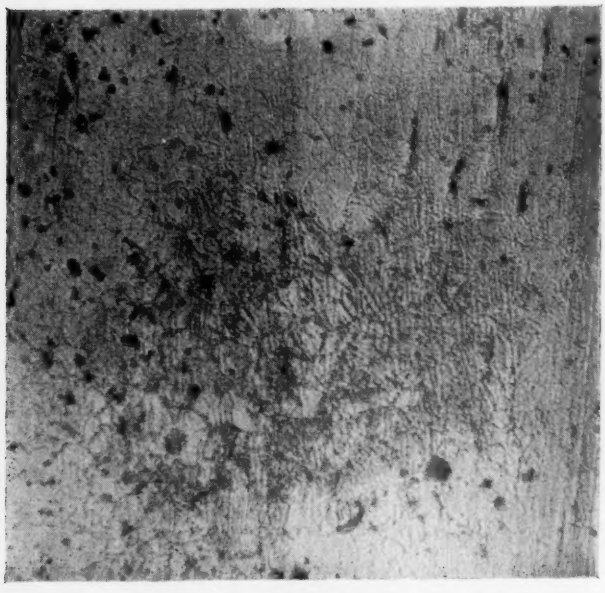

FIG. 4. Start of gross breakdown mark. × 220.

FIG. 5. Typical white marks on copper anode. × 75.

shows what appears to be the start of a breakdown mark containing deep craters and the start of preferential etching. Preferential travel of an arc on an etched cathode surface has been reported by Wroe[12] but it does not appear to be the same phenomenon.

On some occasions white marks of the same order of size, 10^{-2} cm diameter for the relevant gap setting of 0.0325 cm, as reported by Schwabe[13], were observed as seen in Fig. 5, but in this case breakdown had taken place at 20 kV. These again were made up of lines of craters, which followed the polishing lines, and the usual deep craters surrounded by a lip as shown in Fig. 6. Hough-Grassby[14] has observed innumerable spots about 10^{-2} cm diameter on the anode surface after what seemed to be non-sparking discharges in oil contaminated systems.

Occasionally brown films (about 2.7×10^{-3} by 3.3×10^{-2} cm in size) were found, Figs. 7 and 8. These had quite clear-cut edges and in some cases contained a bluish centre, showing a different thickness of the film, Fig. 7, or as shown in Fig. 8 evidence of gross melting similar to that reported by Schmidt[5].

Brown films were also observed on the cathode, Fig. 9, containing areas where the layer appears to have been stripped off, Fig. 10. Heard[15] has reported that brown rings arose on

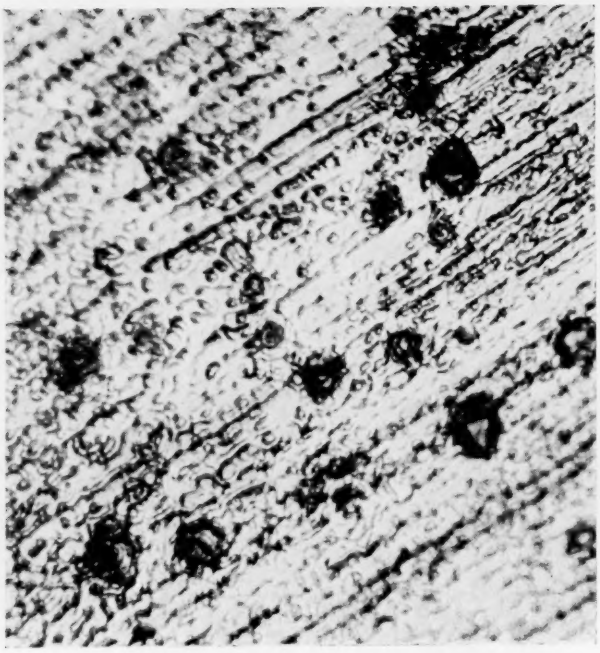

FIG. 6. Shallow and deep craters in white mark. × 630.

FIG. 7. Brown films containing bluish centres on mechanically polished copper anode. × 260.

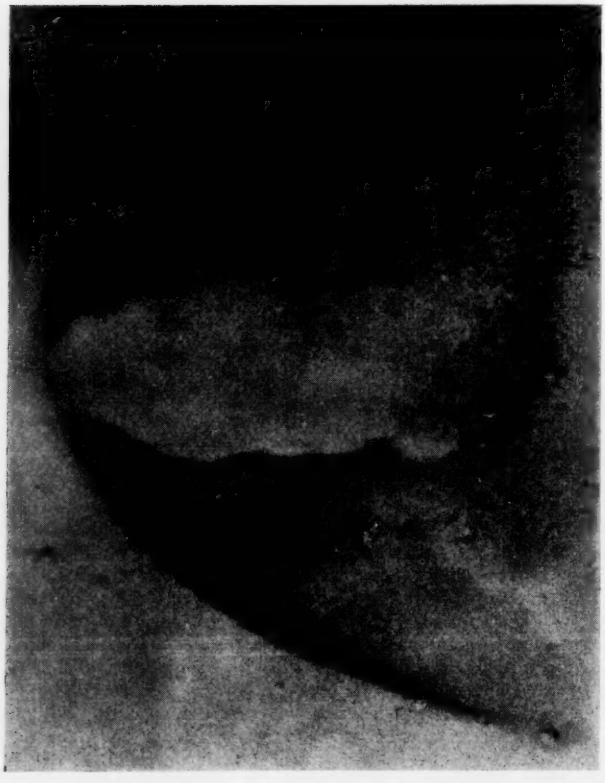

FIG. 8 (*left*). Brown film containing evidence of gross melting. (In this case the surface had been electrolytically polished.) × 1100.

FIG. 9 (*below*). Brown film on mechanically polished copper cathode surface. × 100.

the cathode but never on the anode of an oil contaminated vacuum system. Maitland has previously observed that the cathode became discoloured by a thick oxide film which stripped off in irregularly shaped patches. The cause of such films is not as yet established.

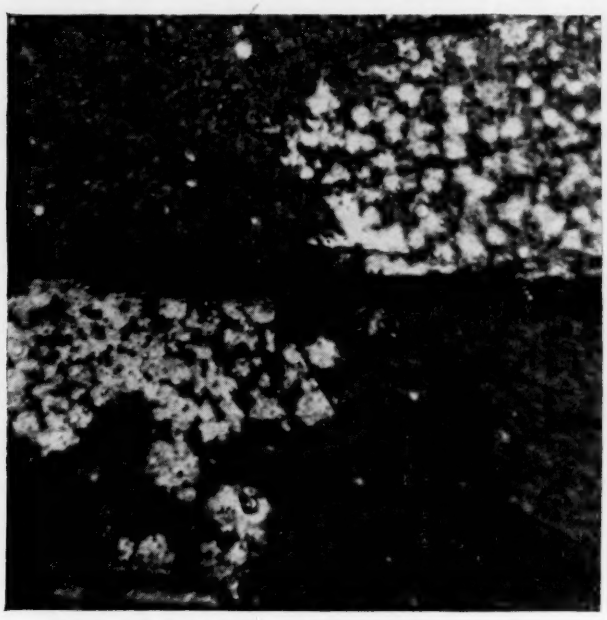

FIG. 10. As Fig. 9. Showing film removal. × 770.

Acknowledgements

I would like to thank A. Maitland for permission to use unpublished results and acknowledge the great help he has given me in preparing this note.

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Self Degassing Oil Manometer

MANOMETER fluids frequently prevent accurate pressure measurements of gases admitted to a high vacuum system. When mercury is used, two major problems must be taken into account:

(1) some experiments fail in the presence of mercury vapor;

(2) pressure changes detectable by eye are limited to 0.1 Torr.

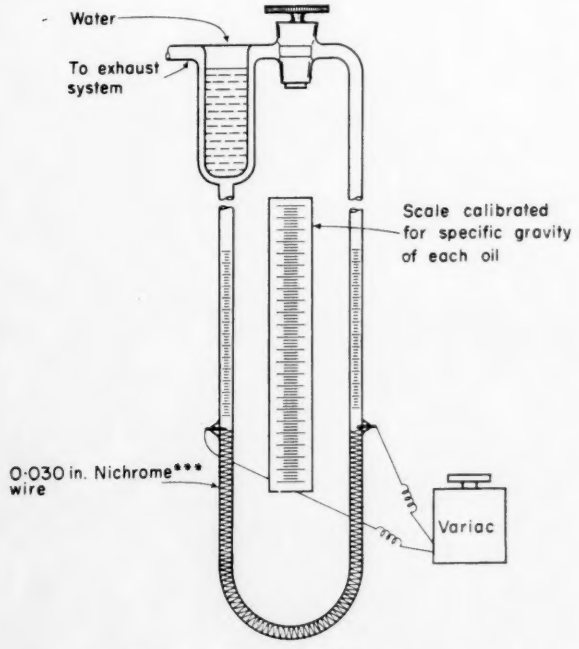

FIG. 1. Self degassing oil manometer.

Low vapor pressure oils (butyl phthalate, Apiezon B* or Octoil-S** diffusion pump oils) may be substituted for mercury. The sensitivity is increased approximately fifteen times, but new limiting factors are introduced. These oils tend to absorb or dissolve the gases under test. Air and water vapor are also picked up in large quantities when the system is opened to the atmosphere. Errors in pressure measurements are a foregone conclusion.

This laboratory designed and fabricated an oil manometer which may be effectively degassed for each test. It has a built-in electric heater coil controlled by a small variac (see Fig. 1). It is designed to evenly distribute the heat over a large section; thus it greatly minimizes the danger of bumping in the oil. A vapor trap, filled with water at room temperature, eliminates the possibility of heated oil vapors migrating to other parts of the vacuum system. No drop in the balanced oil level has been noted over a period of 2 years.

*Apiezon-B = Trademark of Apiezon Products Limited.
**Octoil-S = Trademark of Distillation Products, Inc.
***Nichrome = Trademark of Driver-Harris Co.

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Vacuum Evaporation of Cu, Ag, Sn, Fe and Cr from a TiC Heater

VACUUM evaporation of aluminium metal from a TiC heater was reported by the present authors in this Journal.[1] The same process was attempted in the evaporation of copper, silver, tin, iron and chromium.

The features of the process are as follows : Aluminium metal is batched in an ordinary alumina crucible, into which two TiC bars are inserted so that their ends are in contact with each other. The bars are heated by passing an electric current through them. Aluminium metal wets the surface of the TiC bars freely at high temperature, so it creeps upwards along the bars by the surface tension vaporising quickly. The evaporation can be continued for about an hour until almost the whole of the aluminium content of the crucible is consumed, in which time about 50 g of aluminium are evaporated. The same process could be applied to other metals, and the results of the application are described below. The TiC bar and crucible used in this experiment had dimensions of 70 × 5 × 5 mm and 46 (dia.) × 30 mm respectively, and typical vapour sources are shown in Fig. 1.

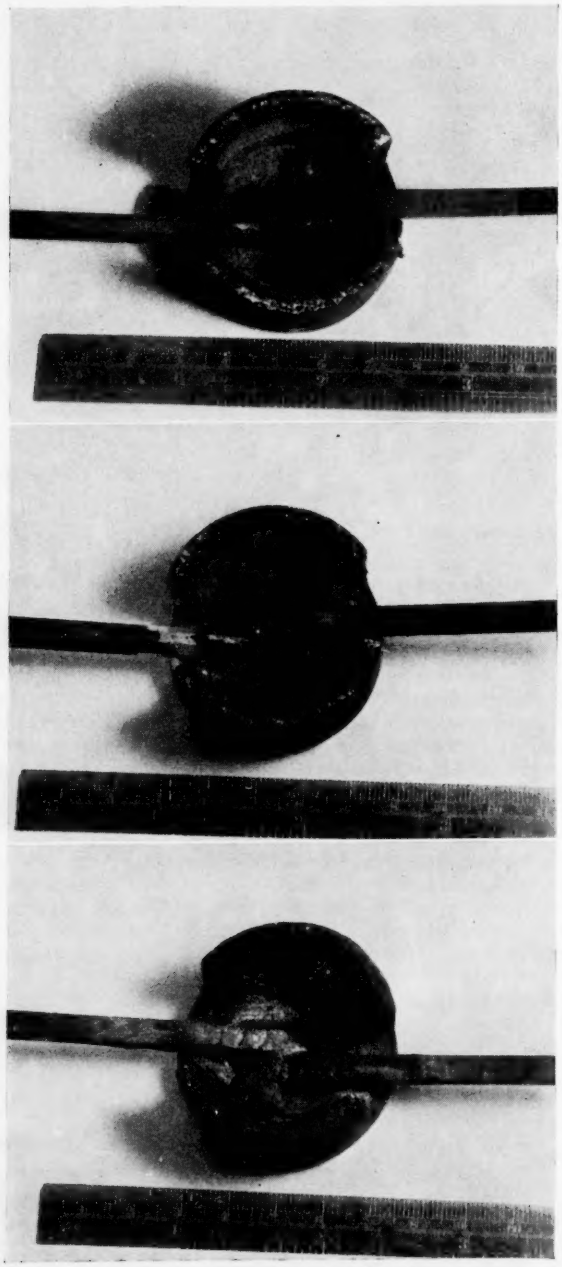


FIG. 1. The evaporation sources of Cu, Sn and Fe, after about 35 g, 10 g and ~2 g (in turn from the top) had been vaporized. (The scale beside the crucible is divided into centimetres on its upper side).

Copper and silver. Copper and silver belong in the IA-group of the periodic chart. Both can be evaporated from a molybdenum boat, but evaporation in large quantities is difficult unless a suitable feeding device is used. By the present method films or foils of arbitrary thickness can be easily obtained. Accordingly applications to printed circuits and so on are expected. The working life of the TiC bar is much longer than is the case with aluminium, because copper and silver do not attack the bar so much as aluminium.

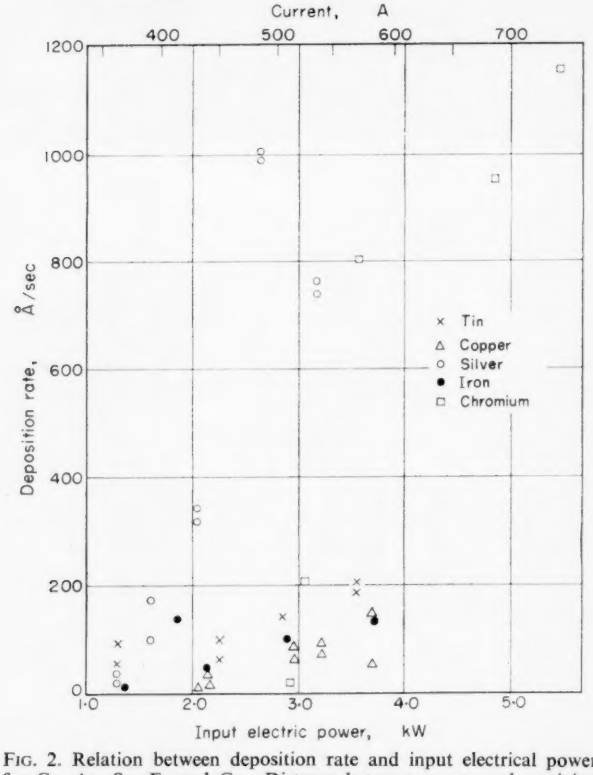
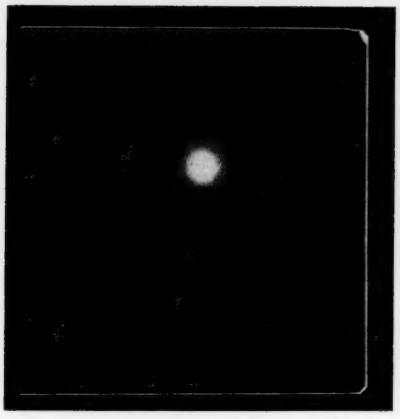


FIG. 2. Relation between deposition rate and input electrical power for Cu, Ag, Sn, Fe and Cr. Distance between source and receiving plate was 115 mm.

Fig. 2 is the diagram showing the relation between deposition rates and input electric power. Fig. 3 is a pinhole figure of the evaporation source by the molecular ray in the case of copper. The figure shows the single source of evaporation in contrast with the dual source in the case of aluminium.[1] The reason why the difference occurs is based upon the fact that copper does not wet the surface of the TiC bar so freely as aluminium.

Tin. Vacuum deposition of tin metal was said to be difficult,[2] but it can be evaporated easily by the TiC method. The TiC bars and the crucible were scarcely attacked, and bars were not wet so freely as with aluminium. Deposition rate of tin was as great as that of copper (Fig. 2).



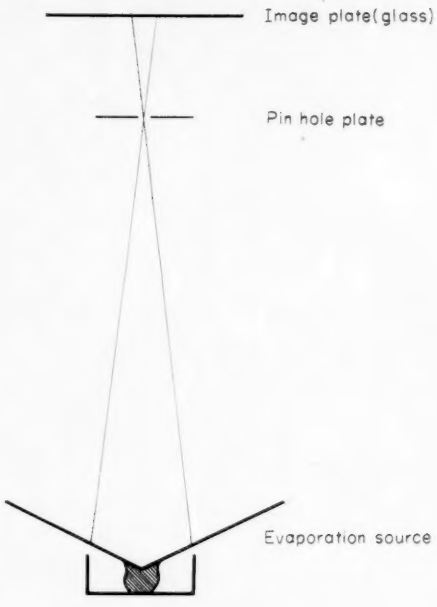


FIG. 3. Pinhole figure of Cu evaporation source. Pinhole diameter, 1.2 mm; magnification, 1/4.5; exposure time, 5 sec; source input power ~2.5 kW.

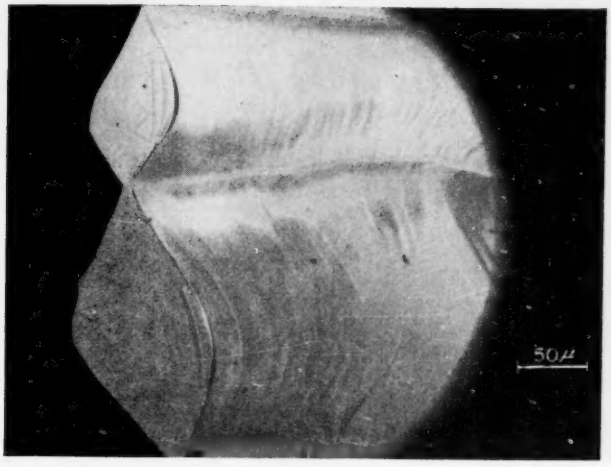


FIG 4(a). Phase contrast micro-photograph of glass surface after thin leaves of glass were sealed off with the iron film. Film thickness, ~5μ; deposition rate, 153 Å/sec.

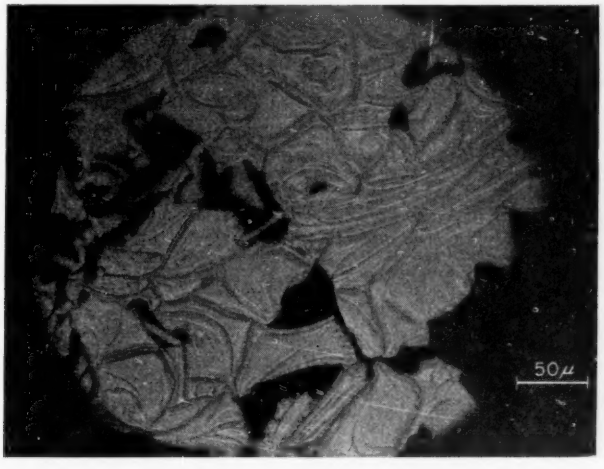


FIG. 4(b). Similar to (a) but with chromium film. Film thickness, ~0.2μ; deposition rate, 221 Å/sec.

Iron. Iron could be evaporated by the TiC method. TiC bars were attacked appreciably by molten iron and parts were scaled off. The iron films thus deposited had great adhesivity to glass. When thick films of iron fell off naturally from glass plates, thin leaves of glass were scaled off attaching to the iron films, leaving a beautiful figure on the glass plate (Fig. 4a). Iron films had the feature that the numbers of pinholes were very much fewer than those of films of other metals.

Chromium. Chromium is usually sublimated from tungsten wire, on which chromium metal has been electroplated. That is, the temperature at which the vapour pressure of chromium reaches about 10^{-2} mmHg, is lower than its melting point (1658°C). In the present case, before melting, deposition did not occur smoothly, but after melting, deposition occurred very rapidly. Ordinary alumina crucibles were heavily attacked by chromium, and a black deposit resulted. Crucibles of pure alumina were not attacked, and evaporation was achieved in these crucibles. Adhesion of chromium films to glass plates is also very excellent (Fig. 4b).

Acknowledgements

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The Creation and Maintenance of Clean Liquid Metal Surfaces

THE cleanness of surfaces is of utmost importance, whenever processes depending mainly upon surface phenomena are considered. The creation and maintenance of clean surfaces is one of the basic requirements in Vacuum Science and Technology, necessary not only for securing the ability to attain very low pressures in a chamber, but also for many processes usually carried out in high vacuum, e.g. evaporation and deposition of metals, electronic processes, etc.

Considerable efforts have been made by authors[1–3] to overcome the difficulties required for the creation of clean surfaces for various purposes. The difficulties exist not only for solids, but for liquids and especially for liquid metals. This is caused in the case of liquid metals mainly by the extremely high chemical activity towards many of the common gases, but may be caused by physical contaminants on the liquid surface.

Thus, Knudsen[3] has found, that the "evaporation coefficient" of a mercury surface decreased to 1/2000 of its value if the examined surface was covered with a visible contamination layer, caused probably by the condensation of the volatile components of sealing wax.

Rossmann and Yarwood[4] have found considerable inconsistency in the results of the experimental determinations of the condensation coefficient of mercury, caused probably by the slight contamination of the mercury surface with carbon dust originating from the containing carbon crucible used. Similar difficulty was experienced by the same authors at relatively high temperatures, in their studies of liquid silver and gold.

In order to secure clean mercury surfaces for his classic experiments concerning evaporation and condensation, Knudsen[3] renewed the surface periodically by dropping a mercury drop from a capillary approximately every 4 sec. The evaporating surface of the drop was evaluated from seventy-two photographs taken during the forming and dropping period.

The following method proved to be realizable for the creation and maintenance of clean surfaces of many metals in the liquid state, functions continuously, and has the additional advantage that it may be applied not only for research investigations, but for industrial processes as well. Moreover, it offers the possibility of creating and maintaining fairly clean surfaces despite the presence of relatively strong contaminating activity.

The liquid metal is permanently forced to stream by a hydraulic pressure gradient developed by an electromagnetic field[5], in a suitable container system, which is partly open at a section where the surface to be created is formed. After passing the exposed surface, the liquid metal returns through a separator (in which the possible contaminations are retained and accumulated) to the electromagnetic transfer device, which transfers the clean liquid metal again to the exposed surface.

The scheme of a realized experimental arrangement of the above method is shown in Fig. 1. The liquid metal is circulated by the electromagnetic pump *P*, transferring it from the bottom of reservoir *R* to the section *A—A* of the piping, which is open at its upper part. The clean surface *S* of the liquid metal is formed at the opening. The metal returns through the separating reservoir *r* into the main reservoir *R*. In this arrangement the surface impurities are supposed to have smaller densities than the liquid metal, so these are accumulated in the upper part of the separating reservoir. The main reservoir may function in a similar way as a separator of contaminations. A pressure equalizer line *E* is applied, as shown in Fig. 1.

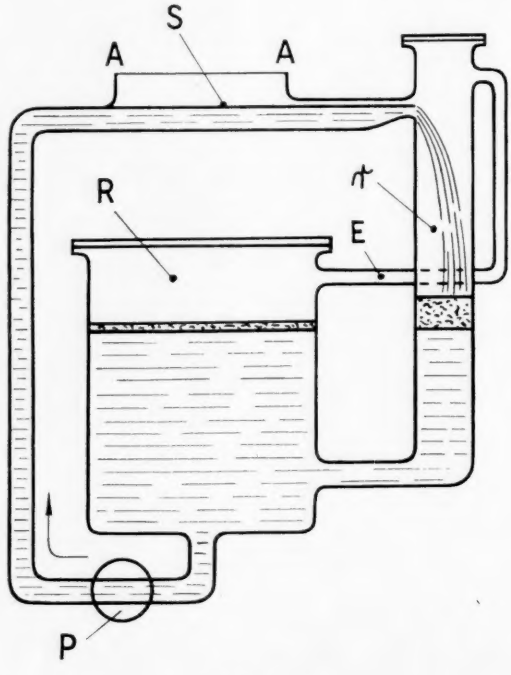

FIG. 1.

The realized system in operation already and to be described in detail in the future[6], was designed to create clean surfaces of chiefly Zn and Cd for the purpose of evaporation. The proper temperatures of the system are achieved by resistance heating, conductive and radiative heat transfer. Mild and stainless steels were used as the main structural materials.

The above equipment is enclosed in a high vacuum chamber, but if the investigation of the surface, or the desired process

demands it, the created surface or the whole equipment may be placed into an inert or reactive atmosphere.

At the beginning of circulation the liquid metal will be very effectively outgassed, if the surface S is exposed to an atmosphere at low pressure. The liquid metal surface might alternatively have been produced, of course, as the free surface of a falling film or as a free beam.

The system is characterized by limited lifetime, like all systems operating at high temperatures. The effect of corrosion may be essentially counterbalanced, however, by keeping only the surrounding of the section A—A at the desired high temperature, and by replaceable design of the strongly attacked parts.

The realization of the principle of the above method may be achieved in many various ways. In any case, however, the governing viewpoint of the design is the consideration of the corrosion of the container system including the electromagnetic pump, held at the required temperature of the liquid metal.

Applying common structural materials, e.g. various steels and stainless steels, it is possible to produce without much difficulty clean surfaces of many elements, e.g. Li, Na, K, Rb, Cs, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, Bi, and many alloys, the highest applicable temperature depending in each case upon corrosion.

Applying refractory metals and their alloys, graphite, ceramics, and by suitable design of the electromagnetic pump, the number of metals/alloys applicable for handling, and the operating temperature may be substantially increased.

The clean liquid metal surfaces created and maintained by the described method may be applied[6] for investigations in surface physics and surface chemistry, and for many practical purposes as well. Some of these are : continuous evaporation, distillation of metals or alloys, desorption of gases from metals or alloys, continuous sorption of certain gases for various purposes, etc.

Acknowledgements

I am grateful to Professor P. Gombás, Director of the Institute, for kindly enabling me to carry out the work, and to Messrs. A. König and J. Antal for valuable discussions.

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Vol. 11 1961

Cracking of High Vacuum Grease and Wax Vapours on Hot Platinum

EXPERIMENTS have been made to measure the rate of production of gases by the cracking of Apiezon N grease and W40 wax vapours on hot platinum. This note reports the results obtained.

The measurements were made in a static vacuum system, in which the background rate of desorption was about 10^{-6} lusec. An electrically heated platinum strip was mounted from copper leads inside a fused silica tube. The wax or grease under test was spread over the inside surface of the silica tube, which was kept cool by an air blast. The gases produced by the cracking reaction were collected in a " break seal " type of glass container for subsequent mass spectrometric analysis.

	Apiezon N grease	*W40 wax*
Filament temperature (°C)	1000	1000
Run duration	24 hr	2 hr 10 min
Rate of production of gas (μl/cm²/hr)	0.5	20
Analysis (Volume per cent)		
Hydrogen	79.2	48
Nitrogen or carbon monoxide (probably carbon monoxide)	20.2	
Oxygen	0.31	0.5
Ethylene		24
Propene		10
Butene		4
Acetone		14

To obtain reproducible results it was necessary to evolve the more volatile components from the sample under test by keeping it under vacuum, with daytime pumping only, for at least 12 days.

After a 20 hr outgassing (330°C) of the container, the platinum filament was heated to 1000°C until sufficient gas had been collected. During collection water-vapour was removed by a phosphorus pentoxide trap. The results of the mass-spectrometric analysis are given above.

The measured rate of production of gas from Apiezon N grease is probably too high : Incomplete removal of water-vapour by the phosphorus pentoxide would allow some decomposition on the hot platinum to produce oxygen which would react with the copper leads (temperature ≃250°C), the hydrogen remaining in the gas phase. In the short W40 wax experiment the acetone was probably produced by a reaction of methane on the oxidized copper leads, whilst in the longer Apiezon N grease experiment it is possible that further reaction on this oxide layer produced carbon monoxide.

It would appear that on prolonged exposure to hot platinum the wax and/or grease vapour would eventually decompose to hydrogen and carbon monoxide in the presence of water-vapour. Presumably in the absence of water-vapour the final products would be hydrogen and carbon.

Acknowledgement

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H. J. ALLSOPP

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Book Reviews

MOLECULAR DISTILLATION (Monographs on the Physics and Chemistry of Materials). By G. Burrows. Clarendon Press; Oxford University Press, 1960, pp. 224, 35s.

IN the 35 years of open path distillation, this is the first and only book to appear dealing solely with the molecular still. Written by an engineer-physicist who has been in the development from the beginning and in the laboratory of origin, the 200 pages, ten tables and forty figures speak with unchallenged authority.

The approach is scholarly rather than historical, Chapter 1 opening with the kinetic theory of gases as related to distillation. The Knudsen-Langmuir rate equation, which is the currency of the molecular still, is developed in Chapter 2 with a discussion of the evaporation coefficient, f, which reduces the maximum intrinsic rate of evaporation, a, always to below the calculated maximum. The physical reasons for this—relative shape of evaporator and condenser and density of emergent vapour—are worked out elaborately, leading to Ronald Frazer's generalization that in rapid unobstructed path distillation the molecules re-entering the evaporating surface tend to a maximum of 50 per cent. At generally useful rates the percentage is smaller, approaching zero, i.e., $f = 1$, from a cylindrical evaporator within a larger condensing cylinder when the saturation pressure (rate) is below 0.002 mmHg.

Chapter 3 presents Raoult's and Henry's laws, the Rayleigh equation and standard methods of predicting, performing and interpreting *batch* distillations under "molecular" conditions. The next chapter makes brief mention of vacuum pumps, pressures required and obtainable, gauges and other vacuum aids, supported by use equations, calculations of speed and throughput which will be useful to the designer.

The photographs of industrial stills in Chapter 5 are impressive but hardly informative though the companion section on details of construction, choice of metals, will aid the professional engineer. From this introduction to apparatus in Chapter 6, we jump back again to comparisons of vapour pressure curves on the Cox chart, relation between chemical composition and vapour pressures, properties of liquid films, spread by gravity, and other means (wiping and centrifugal force), calculations concerning dissolved gases and their means of removal; indeed everything needed to get ready for a distillation.

The story now jumps back again (Chapter 7) to apparatus, which ranges from the simple laboratory jam-jar still all the way to batteries of commercial centrifugals linked in countercurrent flow for fractional distillation. Chapter 8 deals with methods of evaluation, plate efficiencies and an account of that trusty mixture EHP–EHS (ethyl hexyl phthalate and sebacate) which regrettably remains our limited yardstick of molecular still performance; Bradley and Shellard's graphical treatment is included.

The section the author is most qualified to write is perhaps the least satisfactory. The *history* of the vacuum still is the key to its evolution and its future improvement. In the abbreviated treatment of the first and last chapters, the uninitiated reader is not told why he should need a vacuum still, and there is a myopia that allows the fly on the Manchester window pane sometimes to obscure some very sleek cattle on the distant plain. A minor example is the fractionating pump, p. 64 (after Burrows) which actually was invented and first published by Malter of R.C.A. These are minor criticisms; and if the author has not elected to feature the background of the art in the limited space available, he is entirely within his rights. What he has written is good, very, very good and unique—indispensable to all concerned with the art of the high vacuum still, including particularly your hypercritical reviewer.

Future editions would benefit from a glossary of symbols and a bibliography rearranged alphabetically.

K. C. D. HICKMAN

SURFACE MICROTOPOGRAPHY. By S. Tolansky. Longmans, Green, London, 1960, pp. vii + 296, 55s.

PROFESSOR TOLANSKY has taken in hand one particular application of optical interference, the contouring of surfaces, and by using science to perfect it and imagination to extend its scope, has raised its status as a means of surface examination to a level at which, in one dimension, it stands with the electron microscope. One can imagine the stodgy treatise which some writers might have made of the subject but in this book the author's informal style leavens the page and his enthusiasm fires the reader to reach for his microscope and the simple apparatus with which the fringes and contrast patterns are generated. The book is unusual in that the adaptation of multiple-beam interferometry to surface microtopography and all the applications described are the work of the author and his student collaborators.

The precision of the method depends upon very carefully controlled interference induced by multiple reflections between the surface under examination and a nearly opaque flat reflector laid over the surface. A detailed description of the apparatus and conditions required for the production of very sharp fringes leaves little room for error on the part of the practitioner; the author does not hesitate to reiterate the warning that unless the correct conditions are strictly applied the advantages of the method are lost.

Monochromatic Fizeau fringes are sharpened by the multiple reflection method to a degree which allows sub-division of the fringe spacing to a few parts in a thousand; variations of 10 Å in the surface profile are thus measurable. When the structure of a surface is complex the spacing of the fringes giving this great "vertical magnification" will be too wide to make possible a synthesis of the whole surface structure but in these cases it is found possible to build up a picture of the surface by a 2- or 3-stage process. The semi-reflecting flat is first adjusted to be parallel with the general level of the surface. This makes the intensity distribution across a fringe extremely sensitive to slight changes of level, and with a light source such as an un-filtered mercury discharge lamp, the whole surface can be rendered in "interference contrast" and photographed. Ordinary Fizeau fringes can then be superimposed on the photograph (by changing the source and the tilt of the optical flat) to provide quantitative values for the continuous relief pattern. Some fine photographs of this cross-fringe system are given.

Fringes of equal chromatic order have also been introduced by the author. The fringe pattern is formed in white light and dispersed by a spectrograph; this system has several advantages over the Fizeau system, notably that the fringes are inherently sharper and measure the profile along a defined straight line, and the direction of the curvature of the fringe (i.e. towards

red or violet) indicates the direction of the slope of the surface. Magnifications of a quarter of a million are achieved, so that vertical distances of a few Ångström units can be measured.

The description of these three major methods and of various modifications of them occupies about one-third of the book and covers the same ground as the author's earlier book *Multiple-beam Interferometry* (1948). The remainder is given to a description of researches into surface formations and deformations. Taken as a whole, these are primarily illustrative of the virtuosity of multiple-beam interferometry and anyone wishing to make full use of the methods would do well to study all the photographs and the commentary on them. The results themselves will be of interest to specialists and with this in mind the author has arranged the subjects treated into groups: topography of crystal surfaces; crystal cleavages and etch figures; crystal oscillators (a study of the vibration modes of quartz crystals); surface deformations including the indentations of hardness tests; distortions due to abrasion, impact, polishing and sawing.

The distribution of the 359 photographic plates among the text makes reference to them easy but imposes the use of art paper for the text as well; though the eye is soon irritated by the gloss, perseverence is well rewarded.

K. M. GREENLAND

WERKSTOFFKUNDE DER HOCHVAKUUMTECHNIK. Vol. I.—METALS AND MATERIALS EXHIBITING METALLIC CONDUCTION. By W. Espe. VEB Deutscher Verlag der Wissenschaften, Berlin, 1959, pp. 916.

WHEN I started research work in vacuum physics in 1936, I found the existing textbooks on vacuum technique far from helpful and it was a genuine revelation when I came across the original "Espe and Knoll", finding a whole range of carefully described techniques which were largely unknown in England except in a few very professional valve laboratories. Espe and Knoll continued to be a source of inspiration to me and many others until the period in the middle of the war when Anglo-American vacuum techniques outstripped those of Germany. However, until the present day I have made regular use of my copy and have used it to instruct engineers in training.

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Recently, a revised version has appeared in English under the names of Knoll and Kazan but, unfortunately, this is by no means so authoritative as was the original in its heyday. Espe, now working in Czechoslovakia, has independently prepared his version and it is the first volume (of three proposed) of this book which is now under review.

One must first comment that the present volume takes over 900 pages to discuss matters which went into about 160 pages in the 1936 version. The text is very lavishly embellished with tables and illustrations, the illustrations being mainly graphs of the physical properties of the metals under discussion but also including many examples of applications of the materials in apparatus. A number of these pictures are reproduced from the 1936 edition and are therefore rather dated. A few can be criticized for conveying nothing more than a general impression of the external appearance of some particular embodiment, e.g. the r.f. heaters on p. 711. On the whole, the illustrations do serve a very useful purpose and are well chosen.

The text is divided into nine chapters with the following titles (page numbers are approximate):

1. Preface.
2. Metallographic introduction. 15 pp.
3. Refractory metals and alloys. (W, Mo, W–Mo alloys, Ta, Ta–W alloys, Nb, Rh.) 140 pp.
4. Noble metals. (Pt and alloys, Pd and alloys, Rh, Ir, Os and Ru, Au, Ag, Ag alloys.) 50 pp.
5. Base metals. (Ni, Fe, Cu, Al, Be.) 130 pp.
6. Base metal alloys. (Fe alloys, Ni alloys, Cu alloys, base metal–refractory metal alloys, composite materials, e.g. Dumet and the like.) 140 pp.
7. Rare earth metals. (Zr, Ti, Th and brief notes on others.) 80 pp.
8. Various metals and graphite. (Mg, Ba, Sr, Ca, alkali metals, Hg, C). 80 pp.
9. Special fabrication techniques for vacuum metals. (Shaping, outgassing, surface cleaning, jointing, plating.) 250 pp.

The general plan is to describe for each metal the occurrence in nature, method of preparation, fabrication into commercially available forms, powder, sheet, wire, etc., physical constants in great detail with tables and graphs, uses of the material in vacuum apparatus and a very complete list of references. Each section is therefore self-contained and references for further reading are easily found. The units are given, of course, in the c.g.s. system which probably will trouble Anglo-American engineers.

This material is all excellent. It reflects both the care and accuracy of the continental metal extraction industry by using much data from Heraeus and from *Metallwerk Plansee* and the advances made in America and England in the last 20 years. However, in spite of the very elaborate coverage there are some important omissions. The most important is the limited discussion of stainless steel, which, especially in the non-magnetic forms, is nowadays a very important vacuum material. Data on the properties of the more important commercial alloys and on fabrication and jointing techniques would be most welcome in view of the difficulties which exist. Less important but still noticeable is the relative paucity of the information on Cu–N alloys where one particularly misses any identification of those alloys best known in England and America. By contrast the attention paid to chrome–iron alloys, never very important in Anglo-American technology, seems excessive.

Professor Espe has obviously spent much time in searching the Anglo-American literature but even so his chapter on special techniques has several serious omissions—examples of this are frame grids not described, spark machining not mentioned, few details of argon or helium arc welding. The cleaning processes described lean more heavily on the use of chemical baths and solvents than one would like, at least for long life valves and the use of high purity deionized water does not seem to be mentioned. Also, I could find nothing on ultra-sonic cleaning. I found the tables of methods of joining one metal to another (pp. 793–809) to be most interesting and useful.

At this point I think I have said enough to indicate the general excellence of the book. It is one which should be available in every laboratory undertaking serious vacuum work. It should be said that the German is simple and clear and that one can get a great deal of information even if one only knows the German terms for the more important physical properties. Therefore, monolingual English engineers can extract a good deal of value from it. It is a sobering thought that Professor Espe says that he teaches most of this material in courses on vacuum technology in Bratislava and Prague.

A. H. W. BECK

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Organisation internationale pour la Science et la Technique du Vide

International Organization for Vacuum Science and Technology

Internationale Organisation für Vakuum-Physik und -Technik

ASSOCIATION SCIENTIFIQUE

30, avenue de la Renaissance, Bruxelles 4, Belgique

Président :
Prof. Dr. E. Thomas

Secrétaire administrative:
Mme A. De Henau

2e année	**BULLETIN D'INFORMATION No. 9 - 10**	**Novembre 1960-Février 1961**
2nd year	**NEWS BULLETIN No. 9 - 10**	**November 1960-February 1961**
2. Jahrgang	**INFORMATIONSBLATT Nr. 9 - 10**	**November 1960-Februar 1961**

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2. Jahrgang | INFORMATIONSBLATT Nr. 9 - 10 | November 1960-Februar 1961

EDITORIAL — LEITARTIKEL

Nous souhaitons que l'année 1961 soit favorable à nos membres et à tous ceux qui veulent bien soutenir notre action. Nous continuerons nos efforts en vue de réaliser les buts que nous ont assignés les fondateurs de l'Organisation.

Nous avons le ferme espoir qu'en 1961, l'OISTV se transformera en une fédération comprenant aussi les spécialistes des pays où n'existent pas de sociétés nationales.

A cet égard, tous ceux qui désirent voir se développer la collaboration internationale en science et technique du vide liront avec beaucoup d'intérêt le communiqué de presse qui suit.

*
* *

We wish a prosperous 1961 to all our members and those who are supporting our action. We shall pursue our efforts in order to realize the aims which have been assigned to us by the Organization's Founders.

We firmly hope that in 1961, the IOSTV will be changed into a Federation including the specialists of countries where national bodies do not exist.

In this respect, all the persons who wish an expansion of the international collaboration in vacuum science and technology will read with great interest the following press release.

*
* *

Wir bringen hiermit den Wunsch zum Ausdruck, dass das Jahr 1961 für unsere Mitglieder und für alle diejenigen, die unsere Tätigkeit unterstützen wollen, einen günstigen Verlauf nehmen möge. Wir bleiben weiterhin bemüht, die Ziele zu erreichen, die uns die Gründer unserer Organisation gesetzt haben.

Wir haben die feste Hoffnung, dass aus der IOVPT im Jahre 1961 eine Föderation gebildet wird, in der auch die Fachleute derjenigen Länder Aufnahme finden können, in denen keine nationalen Verbände bestehen.

Daher werden alle die, die den Wunsch haben, dass sich die Entwicklung der internationalen Zusammenarbeit in der Vakuumphysik und -technik weiterentwickelt, die nachfolgende Pressenotiz mit grossem Interesse lesen.

*
* *

I. Communiqué de presse
Press release
Pressenotiz

Par son activité, l'Organisation Internationale pour la Science et la Technique du Vide (OISTV) a favorisé l'établissement d'un nombre croissant de sociétés nationales du vide. Cependant, il est apparu que les statuts originaux de l'OISTV ne conviennent plus à une fédération internationale de telles sociétés nationales. En conséquence, des membres de différentes sociétés nationales et des représentants du Comité exécutif de l'OISTV se sont réunis à Cologne le 27 janvier 1961, à titre non officiel, pour examiner les démarches à faire en vue d'établir une fédération internationale acceptable aux différentes sociétés nationales.

En attendant la publication du compte rendu de cette réunion non officielle, tous les participants ont estimé que les spécialistes du vide seraient heureux d'apprendre sans délai que la réunion n'a donné lieu à aucune difficulté et que le principe de la méthode susceptible de conduire à l'établissement d'une fédération internationale a été envisagé avec confiance.

*
* *

The activities of the International Organization for Vacuum Science and Technology (IOVST) has encouragingly led to the establishment of an increasing number of national vacuum bodies. However, it has become apparent that the original Statutes of IOVST are no longer appropriate for an International Federation of such national bodies. Accordingly an informal meeting was held in Cologne on January 27, 1961, between members of various national bodies and representatives of the IOVST Committee to consider what steps could be taken which would lead to an International Federation acceptable to the various existing bodies. A résumé of this informal meeting will be prepared but it was considered by all present that vacuum workers generally would be happy to learn without delay that no difficulty arose from the meeting and that the basis of a procedure which could lead to the formation of an International Federation was confidently envisaged.

*
* *

Die Aktivität der Internationalen Organisation für Vakuum-Physik und-Technik (IOVPT) hat in ermutigender Weise zur Gründung einer anwachsenden Zahl nationaler Vakuum Gesellschaften geführt. Dabei hat sich herausgestellt, dass die ursprünglichen Satzungen der IOVPT einer internationalen Föderation solcher nationaler Gesellschaften nicht länger entsprechen. Es wurde daher am 27. Januar

1961 in Köln eine zwanglose Zusammenkunft von Mitgliedern verschiedener nationaler Gesellschaften und von Vertretern des IOVPT-Ausschusses abgehalten, um zu untersuchen, welche Schritte in Richtung einer internationalen Föderation unternommen werden könnten, die für die verschiedenen bestenhenden Körperschaften annehmbar wäre.

Ein Bericht über diese zwanglose Zusammenkunft wird vorbereitet ; die Teilnehmer daran hielten es aber für gut, schon jetzt alle Vakuuminteressenten davon zu unterrichten, dass bei dieser Zusammenkunft keine Schwierigkeiten aufgetreten sind und dass eine Grundlage gefunden wurde, mit deren Hilfe die Gründung einer internationalen Föderation zuversichtlich in Angriff genommen werden kann.

*
* *

2. 2e Congrès International de la Science et de la Technique du Vide (1961)

2nd International Congress on Vacuum Science and Technology (1961)

2. Internationaler Kongress für Vakuum-Physik und-Technik (1961)

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Le deuxième Congrès International de la Science et de la Technique du Vide se tiendra au Sheraton-Park Hotel à Washington, D.C. (U.S.A.) du 16 au 19 octobre 1961.

Le Congrès est patronné par l'OISTV et par l'American Vacuum Society (AVS) qui sera également l'hôte.

A cette occasion aura lieu l'Assemblée Générale Statutaire de l'OISTV, ainsi qu'une exposition internationale de matériel de vide qui sera la première du genre organisée aux Etats-Unis.

Les personnes désireuses d'obtenir de plus amples informations au sujet du congrès et de l'exposition sont priées de s'adresser au :

Secrétariat International de
l'OISTV,
30, avenue de la Renaissance,
Bruxelles 4,
(Belgique)

Ci-après, les instructions qu'a établies le Comité du Programme de l'AVS à l'intention des auteurs de communications résidant dans tous les pays, à l'exception des Etats-Unis d'Amérique et du Canada.

Instructions aux auteurs de communications

Les auteurs sont instamment priés de suivre les instructions données ci-après.

Langues

Les résumés et manuscrits seront dactylographiés en français, anglais ou allemand. Les communications seront présentées dans une de ces trois langues.

Date limite pour la remise

—des résumés et synopsis	—1er avril 1961
—des manuscrits	—20 juillet 1961

Ces dates limites doivent être strictement observées.

Acceptations

Veuillez soumettre pour examen par le Comité du Programme, toutes les communications traitant des problèmes du vide. Ceux-ci se rapportent aux sujets suivants : application ; appareillage ; recherche appliquée; études théoriques et fondamentales. Les communications soumises doivent constituer un travail nouveau et original, susceptible d'être présenté devant un auditoire international. Les travaux ayant été présentés ou publiés auparavant ne seront pris en considération que s'ils sont jugés être d'actualité et dignes de figurer ainsi dans les " Transactions de l'American Vacuum Society ".

La réunion de 1961 étant internationale, les acceptations de principe se feront sur la base des résumés reçus. L'acceptation définitive ne pourra se faire qu'après examen du manuscrit complet reçu avant la date limite. Le Comité se réserve le droit de refus si, à son avis, le manuscrit reçu ne répond pas par le contenu et l'intérêt qu'il comporte, aux promesses du résumé.

Un envoi rapide de votre texte ne peut manquer de favoriser son acceptation.

Résumés, Synopsis et Manuscrits

Les communications seront rédigées en anglais, en français ou en allemand. Le Congrès ayant lieu aux U.S.A., la majorité des participants sera d'expression anglaise.

Les auteurs qui exposeront oralement leur communication en allemand ou en français sont priés d'envoyer un sommaire en anglais de leur manuscrit, sans illustrations. Le Comité du Programme distribuera gracieusement des prétirages de ces sommaires.

Vous voudrez bien fournir un résumé de 100 mots et un synopsis de 2½ pages, tous deux en *quatre* exemplaires, à double interligne, sur papier de format 21,5 × 28 cm, avec une marge de 2,5 cm. Le synopsis servira à mettre votre communication à la place qu'il lui convient dans le programme ; vous voudrez donc bien le préparer avec un soin tout particulier.

Vous voudrez bien joindre à votre résumé une note de cinq lignes mentionnant vos titres, fonctions et tous autres renseignements pour que votre président de session puisse vous présenter à l'auditoire.

Deux exemplaires du résumé et du synopsis seront soumis à :

Dr. L. E. PREUSS,
Chairman of
1961 Program Committee
2nd International Vacuum Congress,
Department of Physics,
Edsel B. Ford Institute
for Medical Research,
DETROIT 2, Michigan, U.S.A.

Deux exemplaires du résumé et du synopsis seront envoyés en même temps à votre société nationale ou au

Prof. Dr. E. THOMAS,
OISTV
30, avenue de la Renaissance,
BRUXELLES 4, Belgique

Tous les manuscrits doivent être adressés en trois exemplaires au Comité du Programme (adresse des U.S.A.).

Les manuscrits concis et clairs sont en principe acceptés d'emblée. La longueur d'une communication publiée dans les " Vacuum Transactions de l'American Vacuum Society " est d'environ 7 pages imprimées, ce qui correspond approximativement à 15 pages de texte dactylographiées, non compris les illustrations.

Les illustrations, tableaux et légendes ne feront pas partie du manuscrit mais seront annexés au texte. *Un original de grande qualité* plus deux copies des graphiques ou illustrations sont requis. Les impressions doivent être excellentes. Les graphiques médiocres, les photographies de " prospectus " ou les impressions commerciales ne seront pas acceptées. Il est souhaitable que les illustrations soient présentées séparément de leur légende qui sera annexée (aucune indication ne pourra figurer sur l'illustration).

Veuillez en outre fournir une liste récapitulative des graphiques, tableaux et photographies ainsi que des légendes correspondantes et veuillez indiquer l'ordre dans lequel vous désirez que ces documents soient publiés.

Veuillez noter que votre communication devient la propriété de l'American Vacuum Society et qu'elle sera présentée exactement dans la forme originale.

Des épreuves en placards seront soumises à l'auteur en vue de la correction des erreurs typographiques et de *légères* modifications.

Présentation Orale

La présentation tant orale qu'écrite peut être faite en anglais, en français ou en allemand. Rappelons que les auteurs qui liront leur communication en allemand ou en français sont invités à fournir un sommaire anglais de leur manuscrit (sans illustrations) qui sera ensuite reproduit par les soins de l'AVS pour être distribué aux auditeurs, sous la forme de prétirages.

Le temps accordé pour la présentation orale est d'environ 15–20 minutes et sera fixé définitivement lors de l'acceptation du manuscrit ; de ce temps, 5 minutes seront réservées à la discussion. Les auteurs doivent informer le Comité du Programme de la durée *minimum* requise pour leur exposé ainsi que de la langue dans laquelle ils présenteront leur communication.

Des diapositives d'un format de $3\frac{1}{2}$ in. $\times$ 4 in. et de 2 in. $\times$ 2 in. sont recommandées. En vue d'obtenir des facilités pour toute projection spéciale (film, etc.), l'auteur est tenu d'adresser une demande du Comité du Programme au moment de la présentation de son manuscrit.

Les diapositives doivent être étiquetées (coin gauche inférieur) par ordre. *Les diapositives de qualité médiocre ne seront pas acceptées.*

Veuillez réaliser vos diapositives pour que leur projection sur un écran de 3,50 m $\times$ 3,50 m puisse être clairement observée à une distance maximum de 25 m.

*
* *

The 2nd International Congress on Vacuum Science and Technology will be held at the Sheraton-Park Hotel, Washington, D.C. (U.S.A.), from the 16 to 19 October, 1961.

The Congress is sponsored by the IOVST and by the AMERICAN VACUUM SOCIETY which will also act as host.

On this occasion, will also be held the Statutory General Assembly of the IOSTV as well as an international exhibition of vacuum equipment which will be the first of that kind organized in the U.S.A.

The persons interested in more detailed information are kindly requested to write to the :

International Secretariat
of the IOVST,
30, avenue de la Renaissance,
BRUXELLES 4 (Belgique).

Hereafter the instructions to the authors of papers established by the AVS Program Committee.

INSTRUCTIONS TO AUTHORS

The following contains essential information. It is imperative that these instructions be rigorously followed.

Deadlines and Acceptances

Abstracts and Synopsis	—April 1, 1961
Manuscripts	—July 20, 1961

Deadlines must be observed.

All papers concerned with vacuum are invited for consideration by the Program Committee. This includes a full spectrum of topics of : Application, Instrumentation, Applied and Developmental Research, and Theoretical and Fundamental Studies. Papers submitted should cover new and original work, worthy of presentation before an international audience. Material, which has previously been duplicated in other sources, will be considered only if it is deemed of adequate contemporary importance so as to warrant inclusion in the Transactions.

Since the 1961 meeting is international in scope, acceptances will be made on the basis of the abstract received, subject to the *receipt* of the complete manuscript by July 20, 1961. The Committee reserves to itself the right of reconsideration if the manuscript does not bear out the promise of the abstract. Early submission of texts shall have some bearing on acceptance.

Abstract and Manuscript

Texts may be in either English, French or German. Due to location, the majority of attendees will be English speaking. Authors reading papers in German or French are encouraged to send an abbreviated manuscript in English without illustrations. The Program Committee will provide free preprints of these for distribution.

Authors in the United States and Canada must furnish a 100 word abstract and a synopsis ($2\frac{1}{2}$ page maximum), in triplicate, double spaced, on $8\frac{1}{2}$ in. $\times$ 11 in. bond, with 1 in. margins. The synopsis will be used to properly position your paper in the program, therefore, prepare it with care. Abstracts, synopsis and manuscript may be sent to the most

convenient member of the Program Committee. *Do not write to AVS post office box.*

A five-line paragraph of biographical material (professional) must accompany your abstract for use by your session moderator for your introduction.

Abstracts and synopsis originating outside the United States and Canada are to be submitted in duplicate to the Program Committee (United States address) and simultaneously in duplicate to their National vacuum society or to the IOVST (c/o President E. Thomas). All manuscripts in triplicate are to be sent directly to the Program Committee (United States address).

Concise, lucid texts are most readily accepted. Paper length in the Transactions is up to 7 printed pages. The maximum length is about 15 double spaced typed pages of text, plus illustrations.

Illustrations, tables, and captions are not to be incorporated into the manuscript but collated separately (from the text). *One high quality original* plus two copies of graphs and illustrations are required. Prints must be of a high degree of excellence. Poorly prepared graphs, "catalog" photographs, or prints smacking of commercialism will be cause for rejection. Prints are preferably to be mounted and identifying information attached (no marking directly on the illustrations). A figure list and appropriate captions for graphs, tables, photographs, as you wish them to appear for publication, should be furnished in addition to the individual identification of illustrations mentioned in the preceding paragraph.

Text release by your organization and editing is the responsibility of the author. Your paper becomes the property of the AVS and will be published exactly as received. Galley proofs will be provided the author for correction of typographical errors and for *minor* changes.

Oral Presentation

Oral as well as written presentations may be in either English, French, or German. Authors reading papers in German or French are again encouraged to provide an English condensation of their manuscript (without Figures) which will then be reproduced by the AVS for the audience at your session in the form of a preprint.

The time for oral presentation will be 15–20 minutes and will be fixed at the time of acceptance of manuscript. Of this, 5 minutes may be for discussion. Authors must inform the Program Committee of the *minimum* time required for their lecture.

Slides are recommended only in $3\frac{1}{4}$ in. $\times$ 4 in. and in 2 in. $\times$ 2 in. sizes. It is the author's responsibility to petition the Committee for special projection facilities (movies, etc.) at the time of submission of the manuscript. Slides are to be labelled (lower left corner) in sequence. *Slides of inferior projection quality cannot be tolerated.*

We will have a large auditorium and expect to have a correspondingly large audience present. Your oral presentation should be heard clearly by all. Speaking with good enunciation and with emphasis is necessary to accomplish your purpose. Speak to the man in the back row without dependence upon the microphone. It has been found helpful to rehearse the speech before friends. Study your slides for legibility by projection to 12 ft $\times$ 12 ft size and observed from a maximum distance of 80 ft.

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Der 2. Internationale Kongress für Vakuum-Physik und -Technik wird im Sheraton-Park Hotel in Washington, D.C./U.S.A., vom 16. bis 19. Oktober 1961 stattfinden.

Der Kongress wird von der Internationalen Organisation für Vakuum-Physik und -Technik (IOVPT) und von der Amerikanischen Vakuum-Gesellschaft (AVS), die gleichzeitig Gastgeber sein wird, abgehalten.

Bei dieser Gelegenheit wird die Generalversammlung der IOVPT stattfinden sowie eine internationale Vakuumausstellung, die erste dieser Art, die von den Vereinigten Staaten organisiert wird.

Falls Sie weitere Informationen über diesen Kongress und diese Ausstellung wünschen, wenden Sie sich, bitte, an folgende Adresse :

Secrétariat International
de l'OISTV,
30, avenue de la Renaissance,
BRUXELLES 4
Belgique

Beiliegend finden Sie Hinweise, die das Programm-Kommittee ausgearbeitet hat, mit der Bitte, diese an alle Mitglieder, die Vorträge halten wollen, weiterzuleiten, ausgenommen solche, die in USA oder Kanada wohnen.

Hinweise für Vortragende

Die Vortragenden werden gebeten die folgenden Hinweise zu beachten :

Kurze Zusammenfassungen und Manuskripte sollen in Französisch, Englisch oder Deutsch eingereicht werden. Die Mitteilungen werden in einer dieser 3 Sprachen erscheinen.

Letzter Termin für die Einsendung

—Zusammenfassungen und kurze übersichen —1. April 61
—Manuskripte —20. Juli 61

Diese Daten müssen streng eingehalten werden.

Annahmen

Legen Sie bitte alle Vorträge, die vakuumtechnische Probleme behandeln, dem Programm-Kommittee zur Prüfung vor. Diese sollen sich auf folgende Themen beziehen : Anwendung, Geräte, angewandte Forschung, theoret. Untersuchungen und Grundlagenforschung. Die eingereichten Unterlagen müssen eine neue und originale Arbeit bilden, die geeignet ist, vor einem internationalen Publikum zu bestehen. Arbeiten, die schon früher vorgelegt und veröffentlicht worden sind, werden nur dann in Betracht gezogen, wenn sie als aktuell und wert befunden werden, sie such in den Veröffentlichungen der amerikanischen Vakuumgesellschaft aufzuführen.

Die Zusammenkunft 1961 ist international ; die Annahmen richten sich nach der Basis der erhaltenen Berichte. Definitive Annahme wird nur nach Uberprüfung des vollständig erhaltenen Manuskriptes vor dem oben erwähnten Termin möglich sein. Das Komitee behält sich das Recht der

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Zurückweisung vor, sofern, nach der Meinung des Komitees, das eingegangene Manuskript nicht durch Inhalt und Interesse dem eintspricht, was erwartet wird.

Eine schnelle Ubersendung des Textes kann nur dessen Annahme begünstigen.

Zusammenfassungen, Ubersichten und Manuskripte

Die Mitteilungen werden in Englisch, Französisch oder Deutsch zusammengestellt werden. Der Kongress findet in den U.S.A. statt ; die Mehrheit der Teilnehmer wird englisch sprechen.

Die Mitglieder, die ihren Vortrag mündlich in Deutsch oder in Französisch halten werden, werden gebeten, eine Zusammenfassung ihres Manuskriptes (ohne Bilder) in Englisch zu übersenden.

Das Programm-Komitee wird unentgeltlich Abzüge dieser Zusammenfassungen verteilen.

Bitte senden Sie uns eine Zusammenfassung v. 100 Wörtern und eine kurze Übersicht von 2½ Seiten, beides in 4 facher Ausführung, doppeltem Zeilenabstand, auf einem Papierformat v. 21,5 × 28 cm, mit einem Rand v. 2,5 cm.—

Die kurze Ubersicht soll dazu dienen, ihren Vortrag auf den bestimmten Platz, der ihm in dem Programm zukommt, einzusetzen. Bereiten Sie ihn dennoch mit besonderer Sorgfalt vor.

Ferner fügen Sie bitte eine weitere Notiz von etwa 5 Zeilen bei, die ihre Titel, Funktionen und weiter Auskünfte enthält, damit der Sitzungsvorsitzende Sie der Zuhörerschaft vorstellen kann.

Je 2 Exemplare der Zusammenfassung u. des Kurzberichtes werden

Dr. L. E. PREUSS
Chairman of
1961 Program Committee,
2nd International Vacuum Congress
Department of Physics,
Edsel B. Ford Institute,
DETROIT 2, Michigan, U.S.A.

unterbreitet werden.

2 weitere Exemplare werden zu derselben Zeit an Ihre nationale Gesellschaft
oder an

Prof. Dr. E. THOMAS,
OISTV,
30, avenue de la Renaissance,
BRUXELLES 4, Belgique

geschickt werden.

Alle *Manuskripte* müssen in 3 facher Ausführung dem Programm-Komitee zugesandt werden. (Adresse in U.S.A.).

Manuskripte, die bündig und klar gehalten sind, werden im Prinzip gleich angenommen. Die Länge einer Mitteilung, die zur Veröffentlichung in den Vakuum-Berichten der amerikanischen Vakuumgesellschaft bestimmt ist, ist auf ungefähr 7 Druckseiten festgelegt, was annähernd einen 15 seitigen maschinengeschriebenem Text entspricht, wobei allerdings keine Bilder mit einbegriffen sind.

Die Bildertabellen und Bildunterschriften sind nicht im Manuskripttext einzugliedern, sondern sollen diesem angegliedert werden. Von den Diagrammen und Bildern werden je ein hochwertiges Original und 2 Kopien benötigt. Auch diese müssen von guter Qualität sein. Schlecht hergestellt graphische Darstellungen, Photographien aus Katalogen oder Drucke die handelsähnlichen Charakter haben, müssen zurückgewiesen werden.

Es ist wünschenswert, dass die Bilder getrennt von den Bildunterschriften, die angeheftet werden vorgelegt werden. (Keinerlei Aufzeichnungen dürfen auf dem Bild stehen).

Würden Sie uns bitte ausserdem eine kurze zusammengefasste Liste der graphischen Darstellungen, Tabellen und Photographien, sowie die entsprechenden Bildunterschriften übersenden und ferner die Reihenfolge angeben, in welcher diese Unterlagen veröffentlicht werden sollen.

Notieren Sie sich auch, dass Ihre Mitteilung das Eigentum der amerikanischen Vakuumgesellschaft wird und dass sie in Originalfassung veröffentlicht wird.

Korrekturabzüge werden dem Autor unterbreitet werden, um eventuelle Verbesserungen der Tippfehler und leichte Änderungen vornehmen zu können.

Mündlicher Vortrag

Sowohl mündlich vorgetragene Themen als auch schriftlich eingereichte können in Englisch, Französisch oder Deutsch gebracht werden. Mitglieder, die ihre Unterlagen in Deutsch oder Französisch lesen, werden gebeten, eine englische Zusammenfassung ihres Manuskriptes (ohne Bilder) abzuliefern, die dann von der AVS vervielfältigt wird, um an die Mitglieder in Form von Abzügen verteilt zu werden. Die bewilligte Zeit für den mündlichen Vortrag beträgt ca. 15–20 Minuten und wird endgültig bei Annahme des Manuskriptes festgelegt. Von dieser Zeit werden 5 Minuten für eine Diskussion einbehalten. Die Mitglieder müssen das Programm-Komitee über die mindest erforderliche Dauer ihres Vortrags informieren, sowie die Sprache angeben, in welcher Sie den Vortrag halten werden.

Die Diapositive müssen mit einem Etikett versehen sein (innere linke Ecke). Diapositive mittlerer Güte werden nicht angenommen.

Legen Sie ihre Diapositive so aus, dass eine Projektion auf dem Bildschirm von 3.50 m × 3.50 m klar auf eine Entfernung von höchstens 25 m gesehen werden kann.

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3. Réunions — Meetings — Tagungen

Dans cette rubrique, nous annonçons les réunions consacrées à la science et à la technique du vide.

Ne pouvant reproduire ici toutes les informations relatives à ces manifestations, nous prions nos membres de demander de plus amples renseignements aux organisateurs.

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Under this heading, we announce the symposia being held in connection with vacuum science and technology.

It being impossible to reproduce here all the information relating to these symposia, we request our members to enquire more details from the organizers.

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In dieser Spalte zeigen wir die der Vakuum-Physik und -Technik gewidmeten Tagungen an.

Da wir nicht sämtliche Auskünfte und Nachrichten dieselben betreffend abdrucken können, bitten wir unsere Mitglieder sich wegen umfassenderer Informationen an die Organisatoren zu wenden.

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(a) Symposium on USER EXPERIENCE OF LARGE SCALE INDUSTRIAL VACUUM PLANT, 1st-2nd March, 1961, sponsored by The Joint British Committee for Vacuum Science and Technology, arranged by The Institution of Mechanical Engineers, 1 Birdcage Walk, Westminster, London, S.W.1.

Papers to be presented :

1. Introductory Address by N. A. McNeil.
2. Vacuum Equipment for Consumable Electrode Melting of Reactive Materials, by G. W. Turner and K. Deutsch.
3. Industrial Vacuum Melting Plant, by H. C. Child, H. H. Scholefield and P. M. Gray.
4. Experience obtained by Springfiels on the Application of Vacuum to Fuel Element Production Processes, by A. E. Williams.
5. Applications of Electron Bombardment Heating in Metallurgy, by N. F. Eaton, D. B. Gasson and F. O. Jones.
6. Vacuum Induction Melting, by L. S. Taylor.
7. User Experience of Five-Stage Steam Ejector Vacuum Plan, by J. Hodkinson.
8. Vacuum Requirements for Research on Aerodynamics, by D. W. Holder and L. Bernstein.
9. Plant Capacitor Drying and Impregnation, by F. Moores.
10. User Experience with Large-Scale Freeze Drying Plan for Drying Human Plasma, by G. R. Milne and O. S. Petrie.
11. Design and Operation of Molecular Distillation Plant, by P. Ridgway-Watt.
12. The Use of Vacuum in the Preparation of Veterinary Products, by E. C. Hulse and J. M. Collins.
13. Evacuating Equipment for the Accelerated Freeze Drying Food-stuffs, by J. C. Forrest.
14. Vacuum Annealing of Copper, by A. Mortimore.

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* *

(b) Alloyd Electronics Corporation is continuing with its Third Annual Symposium on Electron Beam Technology. This year's Symposium will take place in Boston on the 23rd and 24th of March.

The Symposium will consist of four sessions. The first two on the 23rd will involve Electron Beam Physics ; and Welding and Refining. The second two sessions on the 24th will include Applications of Electron Beams for Advanced Techniques such as Polymerization, Food Processing and other varied areas ; and Present and Future Applications of Electron Beams to Micro-electronics.

Technical papers will be presented by leading scientists representing organizations working in these advanced areas of electron beam technology.

As in the past, the attendance will be limited so the greatest interchange of technical information will be possible.

For detailed information, write R. Bakish, Chairman Third Alloyd Symposium, 37 Cambridge Parkway, Cambridge 42, Massachusetts. (Press release).

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* *

(c) Die Arbeitsgemeinschaft Vakuum wird ihre nächste Vortragssitzung mit dem Generalthema " Ultrahochvakuum " am 20.4.1961 in Bad Neuheim in Zusammenhang mit der Frühjahrstagung der Physikalischen Gesellschaften Hessen-Mittelrhein-Saar abhalten.

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(d) *Journée du Vide du Printemps*

La S.F.I.T.V. organise le vendredi 21 avril 1961 une Journée Internationale consacrée aux Applications Métallurgiques du bombardement électronique. Elle sera placée sous la présidence de M. J. A. Stohr, Chef du Service de Technologie du Commisariat à l'Energie Atomique.

Programme provisoire :

(1) Compte rendu du 3e Symposium consacré au Bombardement Electronique, tenu à Boston les 23 et 24 mars 1961, par M. J. A. Stohr, représentant de la S.F.I.T.V. au Symposium.

(2) Conférences de MM. :

P. Thome : Notions de thermodynamique sous vide. Avantages et limitations du soudage. Appareillages d'études et réalisations industrielles.

J. Sommeria : Étude et fabrication des canons à électrons adaptés aux différents domaines d'utilisation.

A. Calverley : The purification of metals using Electron Bombardment Heating.

Dr. E. Bas : La microscopie électronique à émission et ses applications à la métallurgie.

Dr. S. Panzer : Soudure et usinage à l'aide d'un faisceau électronique.

Dr. H. Gruber : Installation pour la fusion des métaux par bombardement électronique avec multiples canons électroniques.

B. Tougarinoff : Résultats métallurgiques de la fusion par bombardement électronique du tantale et du niobium.

(3) Colloque, avec la participation des conférenciers et de divers spécialistes, comprenant notamment divers courts exposés complémentaires.

Pour tous renseignements et conditions d'inscription, s'adresser à l'Administration de la SFITV : Mme. J. Mainier, 147, ter A, Bd de Strasbourg, Nogent-S.-Marne (Seine).

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Papers to be published in future issues

K. H. Behrndt and R. A. Jones. A Comparison between the Evaporation Characteristics of a Crucible and a Ring Source.

R. I. Garrod and J. F. Nankivell. Leak Testing of Large Welded Vacuum Vessels.

R. J. B. Hadden and A. Kirk. Leakage within Glass-fibre Reinforced Epoxy Resin Laminates.

H. Schwarz. Low Pressure Limit of Common Gauges.

Y. Moriya. Vacuum Sintering of Quartz Powder and Phase Transformation of Quartz.

J. H. Bloom, C. E. Ludington and R. L. Phipps. The Study of a Continuous Getter at High Ambient Temperatures with Carbon Dioxide.

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Proceedings of the 5th National Conference on

ELECTRON TUBE TECHNIQUES

(September 1961)

Edited by

DAVID SLATER

New York University

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SPONSORED BY THE
WORKING GROUP ON TUBE TECHNIQUES
ADVISORY GROUP ON ELECTRON TUBES
OFFICE OF THE DIRECTOR OF DEFENCE RESEARCH AND ENGINEERING

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Editorial

THIS issue of *Vacuum* contains fourteen papers selected from the Proceedings of the Fifth National Conference on Electron Tube Techniques for their particular interest to workers in Vacuum Science and Technology. The complete proceedings of this conference have been published by Pergamon Press Limited under the title *Advances in Electron Tube Techniques*; for the information of readers who may be interested in this separate publication a complete list of its contents appears on p. 126.

THE Second International Congress on Vacuum Science and Technology takes place in Washington, D.C. on 16-19th October, 1961, in association with the 8th Annual Symposium of the American Vacuum Society. This issue of *Vacuum* includes numerous advertisers' announcements of special interest to participants in the Congress.

A. S. D. BARRETT,
Co-ordinating Editor.

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Tube Techniques

WALTER H. KOHL

Staff Consultant, Microwave Device Operations, Mt. View Components Laboratory, Sylvania Electric Products Inc., Mountain View, California; and
Lecturer, Department of Electrical Engineering, Stanford University, Stanford, California

(a) A Review of its Broader Aspects and Implications

Introduction

Seven years have elapsed since the First National Conference on Tube Techniques was held in this auditorium. After the second conference, in 1954, the decision was made to hold these gatherings every two years, rather than annually. No one can claim therefore that we contribute unduly to the overabundance of technical meetings which has caused some concern in the minds of those who are expected to attend as well as with the respective managements of the sponsoring institutions who pay the fares.

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Nevertheless, it is proper, I think, to take a broad look at Electron Devices Techniques, of which Tube Techniques has become a part, redefine its meaning and scope, and consider the problems which must be solved if this discipline is to make its fullest contribution to the advance of our space-age technology. This review will lead us to consider the various levels of application, the training required by the practitioners of the art, the means available to spread this know-how throughout an organization, and the support required from management to bring about a consistent application of sound principles with a minimum of confusion. Examples will be given of how the solving of problems might best be approached, and concluding remarks will touch on the role which a wider dissemination of knowledge about techniques can play in creating a more sympathetic attitude on the part of the general public toward scientific pursuits in general.

Meaning

What, then, is the meaning of Electron Devices Techniques, or Tube Techniques in particular, on which the main emphasis will be put in the body of this presentation? Do we refer primarily to the craftsmanship of a technician without whose skill a tube can never be built, or do we have in mind the broader understanding which a materials engineer applies to the solution of design problems? Surely the latter assumption is valid and must be elaborated to embrace the first one. The subjects treated at these conferences were always either of a theoretical or a practical nature, both approaches being about equally represented at a given symposium, so that both the technician and the researcher could derive benefit from their respective attendance. One might say, then, that Tube Techniques is a generic term for knowledge of the properties of materials and experience in the use of processes, both being applied to the construction of electron tubes.

Scope

An expert in electromagnetic theory and electron dynamics may demand a geometrical configuration which satisfies a desired potential distribution in space when proper voltages are applied to the elements. This is a mental construct, not a design. The materials engineer will then take over and decide which materials are compatible, how to join them in the most suitable manner to arrive at a structure which can survive critical environments and be made at low cost.

The ideal materials engineer for electron devices would have to be a most versatile man, of broad experience and educational background. He should be sufficiently familiar with electronic theory to understand the principles on which the operation of a proposed design outline is based. For its realization, he must know materials properties as described in the fields of mechanics, metallurgy, chemistry, ceramic technology, high-vacuum technique, high-voltage insulation, surface physics and chemistry, and others. He should also be a diplomat, a psychologist, an accountant, a salesman, in other words a good manager to boot. Obviously, it is impossible to combine all these functions in one person. He needs help.

A number of specialists in the areas just outlined will be called upon to make their contributions to the original design proposal, and the technicians, who are also specialized in various fields, will finally produce a prototype. After necessary changes have been made to optimize performance, the tube may be scheduled for pilot production, and a tube engineer takes over. He will look critically at the cost of production and may have to modify the design to suit his purposes. To do this successfully, he must, in turn, be imbued with " Tube Techniques " in the fullest sense of the word, unless costly failures result. At the same time, all those involved in the original development can greatly reduce time and cost for productization, if they choose their methods with this end-purpose in mind.

Organization

Quite a number of people are now involved in the realization of a common objective. This calls for an organization which requires management. Management is not an end in itself ; it has the task to promote by means of proper organization, i.e. assignment of authority and responsibility, the achievement of a given task with a minimum of friction. It is of course necessary that management itself fully appreciates the meaning of Tube Techniques in the sense outlined above before it can hope to manage it effectively.

To be competitive in the field of tube manufacture, it is essential that proven practices are used and that advantage is taken of the latest advances. Information on such available techniques must be disseminated among all concerned in an organized manner, and old, established procedures continuously scrutinized for possible improvement. Suggestions for such improvements and the introduction of new procedures, should be carefully studied and implemented without delay.

The enforcement of these measures is bound to pay great dividends. Nevertheless, many who have worried about these problems will concur that the achievement of these so desirable objectives is fraught with great difficulties.

To remain abreast of the latest advances in the techniques field requires a continuous survey of the international literature,* extraction and cataloguing of pertinent data, and distribution of such information to various departments. This is a full-time job for a man who is thoroughly familiar with the subject and who has at his command several languages. It requires access to a good library with a competent staff who can take over some of the chores outlined above. All of this costs money.

It is unfortunately true that all published information is several years old and likely to be already superseded by more recent advances. Many of the data are originally presented at meetings of technical societies or symposia. The large attendance at the present gathering, and others like it, attests to the benefit which may be derived from the early disclosure of current work, but the limited capacity of the human mind to take in and digest a mass of data, such as offered during a three-day conference, again emphasizes the importance of follow-up and quick publication.

The next problem which confronts us, once a new approach or a potentially useful new technique has come to our attention, relates to the sales effort required to get it accepted and incorporated in the frequently long-established procedures of doing things. To test a new technique on the production line would definitely be the wrong approach as it might jeopardize the scheduled output.

The best solution to these problems, it seems to me, is the establishment of a separate group which is solely concerned with the investigation of new techniques and not hampered by the demand of meeting a production schedule. Such a techniques laboratory should have its own equipment and facilities and be able to make recommendations for the adoption of improved techniques on the basis of careful tests which have demonstrated their merit. To feed ideas into such a laboratory and thus make its work most effective, requires some organized effort.

One of the first and most difficult steps in bringing about improvements is to see the problem, or pose the question. A staff consultant on Materials and Techniques to whom such inquiries are directed can fulfil a useful function. He should not be tied down by project responsibilities and should have time to go problem hunting and cross the boundaries of the various kingdoms to find out what is going on in the neighboring realm. A valid passport is not sufficient clearance for such ventures. One had better attend the court receptions and send flowers to the queen. Having established friendly relations and, above all, trust, one might then expect unsolicited inquiries for assistance in solving a problem. The main difficulty is to get younger engineers delivered from the idea that they are expected to know all the answers themselves. It requires a certain maturity to freely admit one's ignorance on certain matters ; the consultant himself should possess this quality and pass it on to his clients.

To solve a given problem, the consultant may in simple cases be able to draw on his experience and familiarity with the field. " I remember when we did so and so " is a frequent response. In other cases it may be necessary to live with the problem for a while and let it simmer, so to speak. An answer may be forthcoming in time. Many of the technique problems are so baffling, however, that they require extensive research before a solution is found. If the effort is justified, the techniques laboratory can devote itself to this task.

Examples of problem solving

In looking back over the history of tube technology, examples can be found where the solution of a pressing problem was delayed for many years in spite of the fact that the principle for its solution was already being used in the same area of endeavor, albeit in a camouflaged manner. One such example is the evolution of glass-to-metal seals from the platinum leads used in the early incandescent lamps to Dumet wire seals, introduced by Fink and Eldred in 1911, and finally to the concept of flexible Houskeeper seals, described in 1923, which made possible the construction of power tubes at a time when radio broadcasting was in its infancy and desperately needed just such a breakthrough. The copper-coated nickel-iron alloy wires (Dumet) already relied on the low yield point of copper as a means to release stresses caused by the difference in thermal expansion between the wire core and the glass into which the wire was sealed. To extend this thin coating to a thin feather edge, or a thin disk of bulk copper, required a bold leap in the imagination of the inventor. I wonder whether Mr. Houskeeper (*sic*) thought of it while he was shaving in the morning.

In the area of ceramic-to-metal sealing, the tube industry

*There are now over 50,000 scientific and technical journals, which publish annually about 1.2×10^6 articles of significance for some branch of research and engineering in the physical and life sciences. About 60,000 new science books and 100,000 research reports are published each year. The rate at which these publications grow is doubling about every 20 years.[1]

has relied for some time on two methods, i.e. the active alloy technique and the sintered metal powder technique.[2] With proper care, each of these methods will give satisfactory seals under given conditions, but severe limitations exist, especially when heat shock and ambient temperature reach high levels. When searching for new solutions to this problem, one should not hesitate to look across the fence into the neighbor's garden, so to speak. A good ceramic-to-metal seal must have a unique bond between the two components and possibly a bonding agent which has affinity to both. It so happens that pyrolytic carbon films adhere very tenaciously to ceramics ; they are used for precision high-temperature resistors and also for attenuators in travelling-wave tubes. It also happens that metal carbides are very stable and have good vacuum properties.

One of the commonly practiced techniques for the production of metal carbides consists of mixing carbon black with finely divided metal powder and heating this mixture in a suitable gas atmosphere (hydrogen or carbon monoxide, to which a small amount of hydrocarbons may be added to advantage) at temperatures of the order of 1500°C or less. The carbides of refractory metals are thus obtained by interdiffusion at temperatures which lie much below the respective melting points of the carbides. Solid solutions of two or more carbides exist, and their formation is promoted by the presence of molybdenum carbide. It is thus conceivable that a ceramic-to-metal bond can be established by applying a finely dispersed refractory metal powder to the surface of a pyrolytically carburized ceramic and subjecting it to a heat treatment to bring about interdiffusion.

The electrical conductivity of such carbide systems is reported as being close to that of metals, so that the interface formed between metal and ceramic would not cause unduly high electrical losses when this process is used for the production of microwave tubes.

We have performed some preliminary tests at Sylvania to realize this objective. On firing a coated alumina rod in a wet hydrogen atmosphere at 1350°C for 20 min, the mixture of powders commonly used for metallizing ceramics by the sintered metal powder technique (Mo, Mn, Ti) adhered well to the rod. Subsequent plating with nickel and brazing with copper to a Kovar sheet resulted in a strong joint. How strong exactly, and how resistant to temperature shock and other environmental conditions will have to be established by future tests. Whether this answer is positive or negative in this case is immaterial for the purpose of this discussion. It is the method of approach which is to be highlighted. Many other examples could be given, and some will no doubt occur to you at this moment.

The favorable climate

There is an ever-growing body of literature on the subject of so-called creativity. A recent press announcement[3] states that " With the dedication of a new electronic computer system, California Institute of Technology has taken a big step toward unlocking the secrets of creative thinking ". The departments of Biology and Electrical Engineering will cooperate in this venture which is to result in the training and educating of creative thinkers in all fields. This must include Tube Techniques, and it looks as though our troubles will soon be over.

Before this mechanization of the creative effort has been achieved, it might be well to highlight the conditions which must be satisfied before fruitful constellations of thought can occur. One thing is certain ; one must cultivate the broad approach and be aware of developments not only in a specialized field of endeavor but preferably of those in other disciplines as well. The specialist is thus at a distinct disadvantage. There must be time to read widely, to write, to attend occasional meetings and, above all, there must be time to think. Creative work is not a pastime but an intense intellectual effort interspersed with periods of complete relaxation which may be devoted to marginal reading or any activity which takes the mind off the special problem under attack. It is not easy to approach this atmosphere in the tense hustle that often pervades the industrial development department.

Broader aspects

There is a counterpart of this conflict on a much broader scale which may at least be indicated in this context. The rapidly growing trend of our time to develop ever more specialists threatens the cohesion of our society and leaves behind in a vacuum of suspicion and distrust the great majority of those not inducted into the circle of scientifically trained men and women. As Ashby[4] has put it in one of his Granada Lectures, " Social stratification is becoming extinct ; intellectual stratification is taking its place." To counteract this trend, " The Society for the History of Technology " has been formed in 1958, and its journal *Technology and Culture* made its appearance in January 1960. I recommend it to your attention. To quote Watson-Watt : " We should keep an eye on the Inner Space."

Watson-Watt[5] also emphasized in a recent statement the great need for communication with the general public on matters of science and technology so that the gap to which I just referred can be bridged. A valuable bridge can be built between the man who works with his hands and the scientist who works with his brain by emphasizing the important role which craftsmanship has played in some major advances in science. This can be illustrated by many examples[4] and it will appeal to the common man who often is a craftsman himself, be it only in his spare time. I suggest that we search our memories and put on display the cases where tube techniques have made possible important advances in the art of communication and in research endeavor. I am sure that an interesting television program could be developed on this subject.

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(b) Remarks on a Trip to Europe

Let me now add a few remarks which stem from my visit to Europe early this summer. This was essentially a long overdue vacation trip which I undertook with my wife, but I could not resist the temptation to visit a number of laboratories on the way. We spent two months abroad and passed through Germany, Switzerland, Italy, France, Belgium, and England. I attended the Microwave Tube Conference in Munich and visited some fifteen laboratories.

It would be very difficult to pinpoint any special developments in the techniques field which stand out as major advances that have not been made known to us in this country. At the same time, our contributions are being rapidly applied. A natural curiosity in what the other fellow is doing exists on both sides of the ocean, and there is a tendency on both sides to sit up and take notice of any development that is imported.

Workers in Europe are a little envious of the lavish support which the electronics industry in U.S.A. receives from the Government, and they are grateful for whatever spills over under the NATO label. Essentially, our friends in Europe operate in a competitive civilian market and in some laboratories even research has to pay its way to insure continued support. On the other hand, people in European laboratories are not plagued to the same extent by the uncertainties of possible contract cancellations by military agencies. In Great Britain, substantial funds are made available to universities and industrial research institutes through the Chancellor of the Exchequer on a five-year basis. These allocations are made on the recommendation of several advisory councils and go to individuals or institutions *per se* rather than supporting specific projects with definite objectives, as is the case in U.S. Manufacturers with Government contracts can thus make their plans for a number of years in advance.

It has become fashionable in recent years, and indeed mutually profitable on a long-range basis, to establish listening posts, liaison offices and branch laboratories in Europe to keep abreast of new developments in science and industry and exchange information in a broad area of subjects. Both government and industry have followed this trend.[6, 7] R. M. Burns, Director of the European Office of Stanford Research Institute (Zurich) goes as far as saying : " No forward-looking company can afford to miss what is going on in Europe." I would subscribe to this view. Such relationships must be based on mutual trust and a genuine desire to give as well as to take. Our friends overseas are quite willing to share their experiences with us or to enter into joint programs of development as long as the American partner does not aim at financial control of their company.

Representatives abroad should preferably have some roots in the European theatre and be able to talk the language or the locale which they are visiting. This is not a necessary condition, as a large number of the technical people are able to converse in English, but, if fulfilled, it contributes a great deal to the breaking down of emotional barriers and prejudices.

The wide range of interest in tube development and tube techniques on the other side of the Atlantic and the many important contributions which our friends have made in these areas can be highlighted by several important conferences which have been held in Europe during the past few years. The Proceedings of the First International Congress on Vacuum Techniques, held in Namur, Belgium, in June 1958, have recently been published.[8] I had the pleasure of visiting Professor Thomas, President of the Congress, in Brussels this summer and he asked me to extend his cordial greetings to you. As you know, the International Organization for Vacuum Science and Technology has been founded to perpetuate these symposia and will hold the Second International Congress in Washington, D.C. next year. I hope you have joined this society and support its objectives. As we shall hear a special paper on " Vacuum Techniques in Europe " from Dr. Venema on Friday, I shall not dwell on this subject.

Another very important, successful conference in our area of interest was held in Como, Italy, in 1959, under the Chairmanship of Dr. della Porta, and dealt with " Residual Gases in Electron Tubes and Related High Vacuum Systems." The papers of this conference have appeared in the last issue of *Vacuum*.[9] Again I had the pleasure of visiting Dr. della Porta in Milan this summer and gained a first-hand impression of the scope of the work carried on in his laboratory.

At the Munich Conference in June[10] Dr. Huber presented a review of current tube techniques in Europe. A large part of the content of this talk was presented to us by Dr. Huber two years ago[11] and still is an excellent summary of the present state of the art.

In all the countries which I visited, extensive use is made of getter-ion pumps. Great attention is being given to the role of thin films in vacuum tubes, be it as getters, attenuators, or as part of cathode structures. The quantitative analysis of residual gases by mass spectrometers of one kind or another is practiced widely. One expert in this field emphasized the great care required to get consistent results from an omegatron, where filament temperature and geometry of the system are critical parameters, and exposure to different gases on previous runs may affect subsequent measurements in spite of intervening bakeout.

Spark erosion techniques for the production of microwave delay lines have been further developed so that a web thickness of one mil is possible on interdigital lines ; electron beam machining and welding is coming into use, and ceramic-metal structures for microwave tubes are finding increasing application.

The inadequate supply of suitable materials, such as special ceramics, was mentioned to me in England as a handicap from which development work suffers. Many of the special brazing filler metals do not seem to be readily available. American producers seem to have failed to cultivate these potential outlets abroad.

In conclusion, it may well be said that we are united with our friends overseas by a common set of problems in almost

all spheres of endeavor, be they political, economic, educational or technical. We are separated by different viewpoints which result from the varying emphasis put on a common cultural heritage. Sometimes this bond to the past is a shackle ; sometimes our fanciful wandering without its guiding hand leads us astray. A merging of viewpoints is bound to benefit us all.

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Evaluation of Pyroceram Code 9606 as a Suitable Envelope for Vacuum Devices Operating at High Ambient Temperature

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THE R & D Lab. of the U.S. Army Signal Corps sponsored with Westinghouse the work which will be described.* The objective consisted of an evaluation of Pyroceram Code 9606, one of the glass-ceramics developed recently by Corning Glass Works.

Glass-ceramics which are sold by Corning Glass Works under the trademark "Pyroceram" are materials which have been converted into the crystalline ceramic state from the original glassy state by the use of a heat treatment. By re-heating the glass, crystallites are formed which act as centers for crystal growth as the heat treatment continues. The resultant material is an opaque ceramic of the same shape as the original glass article.

Two types of glass ceramics are now available in commercial quantities, namely Pyroceram Code 9606 and Code 9608. The former has excellent characteristics at high temperature and at high frequencies ; the latter has a very low expansion coefficient and is a general purpose material.

Pyroceram Code 9606 was chosen for this investigation due to its promising characteristics and due to its linear expansion, being close to the refractory metals, such as tungsten or molybdenum.

Permeability

Since the density, and therefore the permeability to gases of crystallized glasses are dependent on composition and heat treatment the first task was then to measure the material for permeability to various gases. In Fig. 1 is shown the system consisting of the Pyroceram Code 9606 specimen which is evacuated by means of a diffusion pump. Gas pressure is monitored with a Bayard–Alpert gauge and a valve permits one to shut-off the pump. The specimen is surrounded by a baffle and heated by means of an electric oven. Several thermocouples measure the temperature. After outgassing specimen and system thoroughly measurements were made of the pressure increase in the closed system (valve was closed) and the gas in question was flooding the heating chamber. The gauge was operated at very low grid currents and in operation only 1 sec was allowed for making a reading, in order to reduce

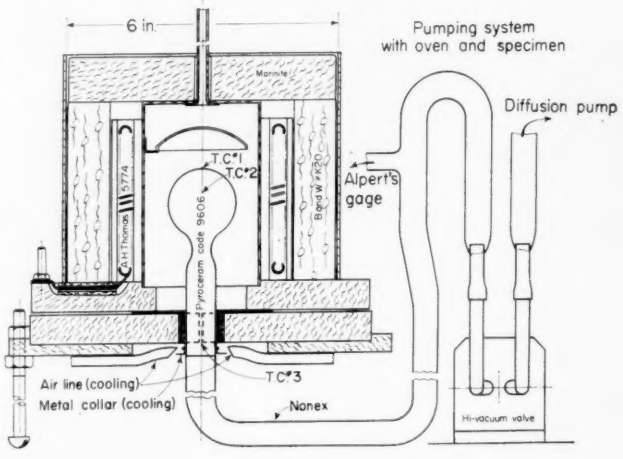

FIG. 1.

as much as possible pumping by the gauge. From data obtained at different temperatures and knowing the physical dimensions of the specimen and the system it was possible then to calculate values of the permeability factor. Corrections were made for the gauge sensitivity to various gases and for temperature differentials of the system.

The observed permeability of various materials to helium is shown in Fig. 2, namely Pyroceram Code 9606, 97 per cent alumina ceramic, No. 7740 and No. 1720 glass ; also a completed tube envelope made of Pyroceram† Code 9606. The value of K of fused silica (quartz) is shown for comparison and was obtained from Norton's work[1] ; the values for No. 7740 glass (borosilicate) and No. 1720 glass (aluminosilicate) agree very well with published data by Norton, Furthermore confirmation was obtained by B. J. Todd[2]. from the same specimen and his measurements were made at 700 °C with a similar method as used by Norton[1]. A completed envelope is also plotted and shows a somewhat steeper slope than is shown for the 9606 material possibly due to the additional influence of the solder glass employed for sealing.

Figure 3 depicts permeability to air for the same materials.

*Contract No. DA-039-SC-75076.

†Labelled in graph "9606 Match-Box Tube".

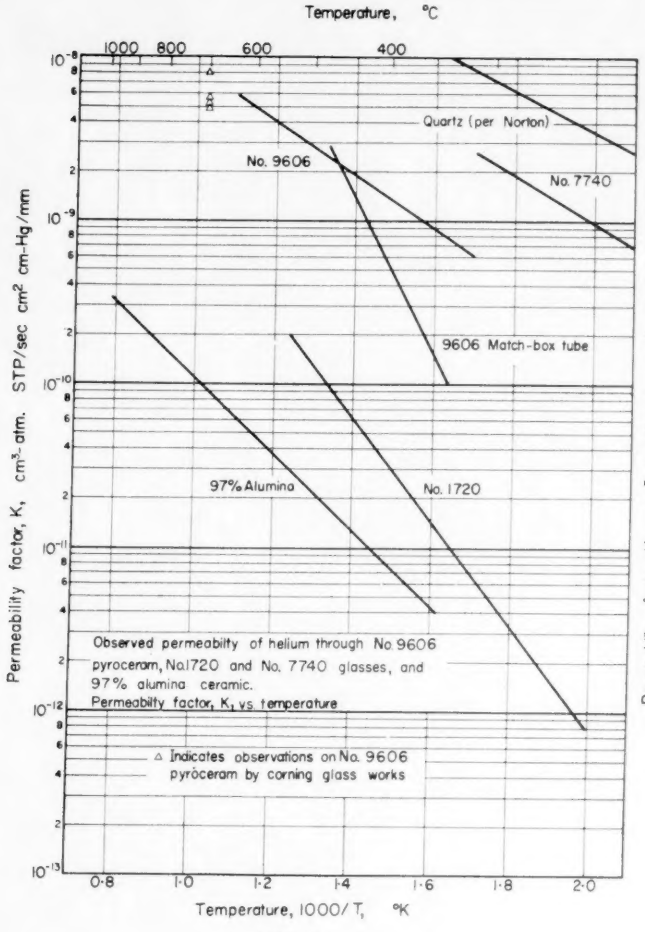
Temperature, °C
1000 800 600 400
Quartz (per Norton)
No. 9606
No. 7740
9606 Match-box tube
97% Alumina
No. 1720
Observed permeability of helium through No. 9606 pyroceram, No. 1720 and No. 7740 glasses, and 97% alumina ceramic.
Permeability factor, K, vs. temperature
△ Indicates observations on No. 9606 pyroceram by corning glass works
Permeability factor, K, cm³-atm. STP/sec cm² cm-Hg/mm
Temperature, 1000/T, °K
0·8 1·0 1·2 1·4 1·6 1·8 2·0

FIG. 2.

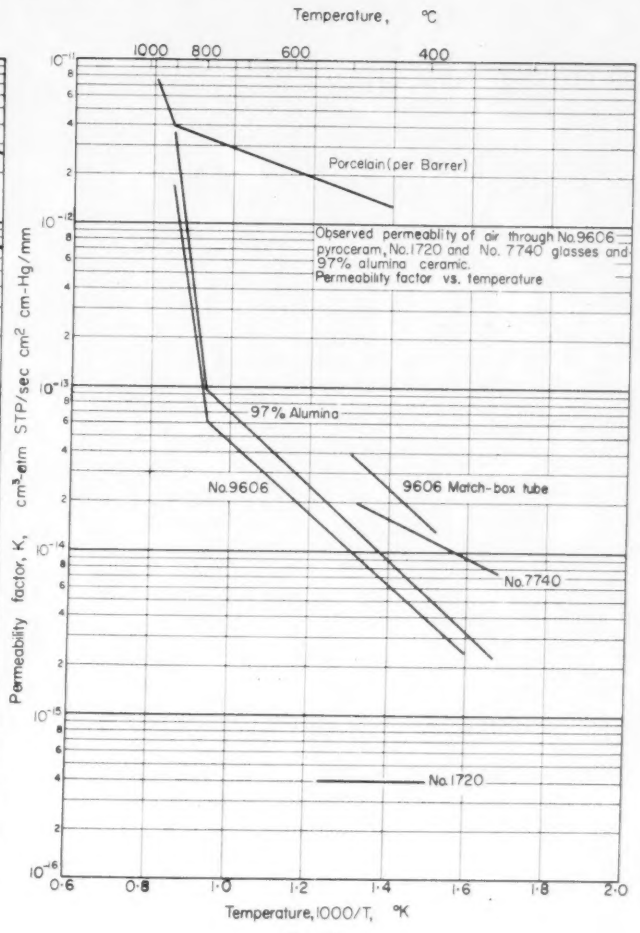
Temperature, °C
1000 800 600 400
Porcelain (per Barrer)
Observed permeability of air through No. 9606 pyroceram, No. 1720 and No. 7740 glasses and 97% alumina ceramic.
Permeability factor vs. temperature
97% Alumina
No. 9606
9606 Match-box tube
No. 7740
No. 1720
Permeability factor, K, cm³-atm STP/sec cm² cm-Hg/mm
Temperature, 1000/T, °K
0·6 0·8 1·0 1·2 1·4 1·6 1·8 2·0

FIG. 3.

For comparison the value of K was calculated from data obtained by Barrer[3] of a material only referred to as " Porcelain ". A change of slope at about 800 °C was found for Pyroceram Code 9606, alumina and porcelain ; this was unexpected but the observed curves are fairly reproducible.*

Release of gases

Since the halogen content of Pyroceram Code 9606 is very low, special procedures were initiated by our Pittsburgh laboratories. A colorimetric procedure was used for the chloride ; fluoride was determined by the red zirconium-alizarin solution.

Halogen content was found as follows :

Chloride, bromide, iodide : 5 parts per million
Fluoride : <20 parts per million

It must be noted that these values represent the bulk of the material. In the actual fabrication of the envelopes a skin is created during the ceraming process, which prevents gases from penetrating the inner surface. An approximate estimate of bulk to skin ratio is 300:1, thus the possible release of halogens would be about 1/300 of the values given above.

Sulphur content in the bulk material was determined in our Chemical Laboratory by dissolving it in acid and distilling off the hydrogen-sulfide (H_2S). The collected H_2S was analysed by the methylene blue method for trace amounts of sulphur. The amount of sulphur was : <25 parts per million. Dalton[4] established for borosilicate bulb glass : 26 parts per million.

Gas evolution rate versus temperature is shown in Fig. 4. These data were obtained by B. J. Todd[5]. Pyroceram Code 9606 compares very favorably with other glasses.

Thermal coefficient of expansion

The thermal expansion curve of Pyroceram Code 9606 is shown in Fig. 5 ; also the expansion of tungsten and molybdenum. The greatest mismatch between the metals and this Pyroceram material is at 180 °C ; however at temperatures above 500 °C tungsten is a better match. At −30 °C the expansion reverses and is at −100 °C equal to the expansion at 25 °C. This behavior is also characteristic of fused silica. Tests conducted in our laboratory with 0.025 in. *dia.* tungsten leads, solder glass and Pyroceram Code 9606 envelopes indicated satisfactory performance of the seals from −76 °C to 750 °C.

*While the permeability for No. 1720 glass is excellent its use in processing at higher temperature is limited, due to the strain point being 672 °C.

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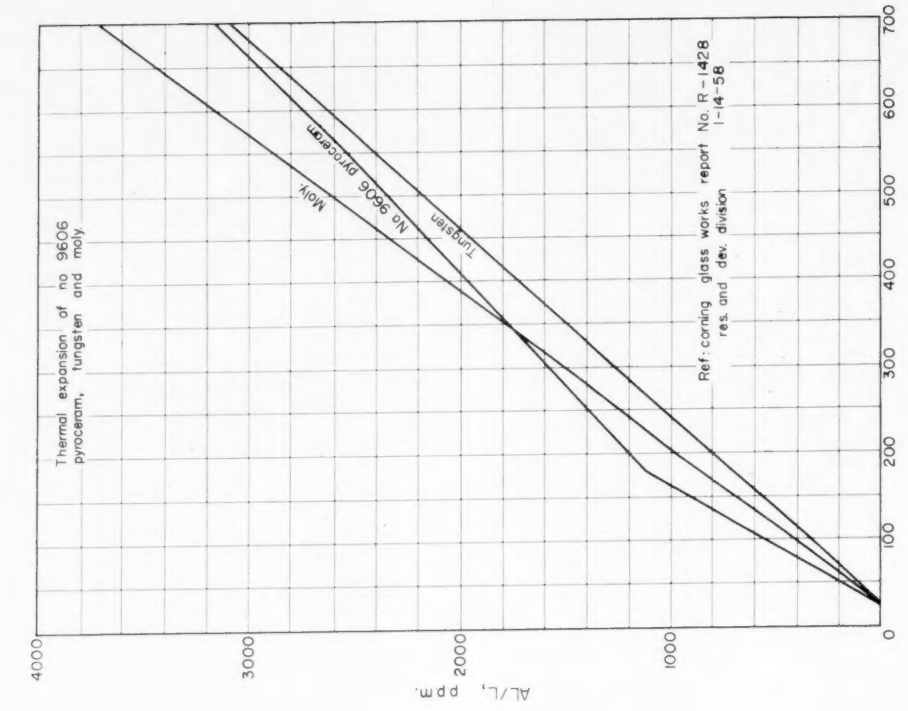
Thermal expansion of no 9606
pyroceram, tungsten and moly
Ref: corning glass works report No. R-1428
res. and dev. division 1-14-58
Moly
No 9606 pyroceram
Tungsten
ΔL/L, ppm.
Temperature, °C
0
100
200
300
400
500
600
700
1000
2000
3000
4000

FIG. 5.

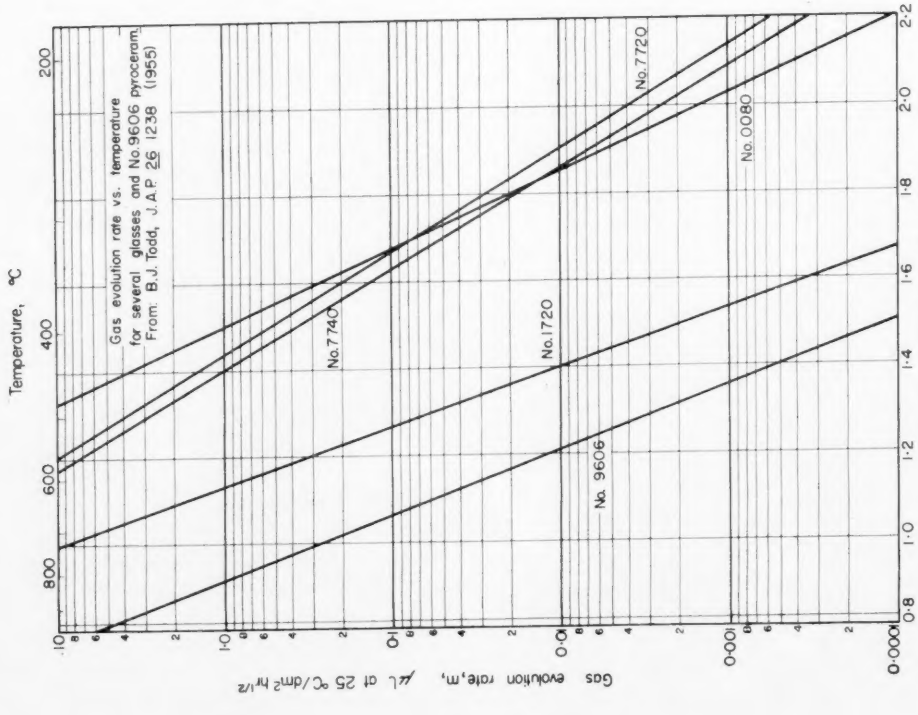
Gas evolution rate vs. temperature
for several glasses and No.9606 pyroceram.
From B.J. Todd, J.A.P. 26 1238 (1955)
No.7740
No.1720
No. 9606
No.7720
No.0080
Temperature, °C
Temperature, 1000/T, °K
Gas evolution rate, m, μL at 25 °C/dm² hr^1/2
200
400
600
800
1·0
1·2
1·4
1·6
1·8
2·0
2·2
0·8
0·1
0·01
0·001
0·0001

FIG. 4.

Successful vacuum tight seals have also been made with Code 9606 Pyroceram tubing and No. 7740 (borosilicate) or No. 7720 (lead borosilicate); it also can be successfully sealed to No. 1720 or No. 1723 (alumino-silicate) tubing.

Volume resistivity at 500°C is about equal to that of No. 7740 at 300°C; it is probable that alumina ceramics have higher resistivity at high temperatures.

The other characteristics of Pyroceram Code 9606 are available from Corning Glass Works[6].

Envelope and its associated parts

Let us consider now the application of this material to a vacuum envelope. Some of the parts which can be successfully produced with Pyroceram Code 9606 are shown in Fig. 6.

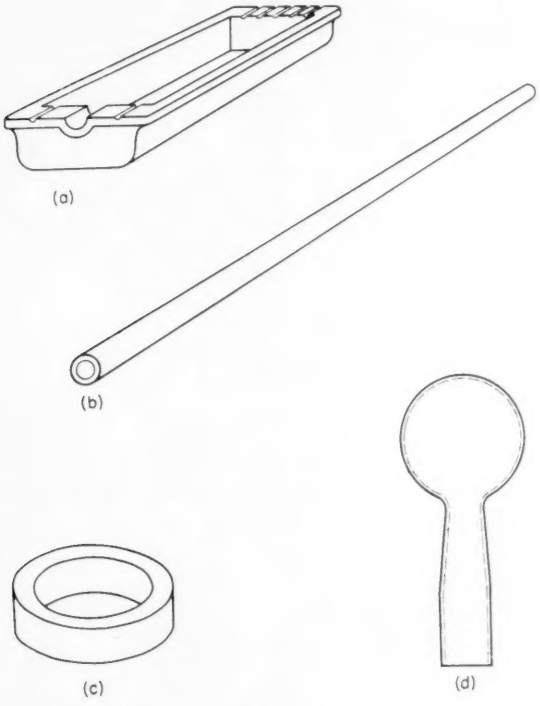

FIG. 6.

Article A is pressed in a mold, B is tubing (also available in rod form) made by well known drawing processes, article C is a ring and article D is a blown specimen, which has a sphere of very thin wall (0.010–0.025 in) and a rather heavy walled stem. The same methods used for making glass articles can be used for Pyroceram. In the ceraming process, which follows the shaping method, minor volume changes (less than 1 per cent) occur. Consequently it is possible to produce articles with this material to very close tolerances, especially since it can be machined in the glassy stage and without the use of diamond tools.

The necessary parts for a specific assembly of an envelope are shown in Fig. 7. The top and bottom envelope (9) are of Pyroceram Code 9606 and pressed in the mold in the glassy stage to identical dimensions. The flanges of the envelope are provided with solder glass Code 7574, grooves are provided in the flanges to receive the lead wires (7) and the exhaust tubulation (11). The tubulation is made of two parts, namely a short piece of Pyroceram Code 9606 tubing

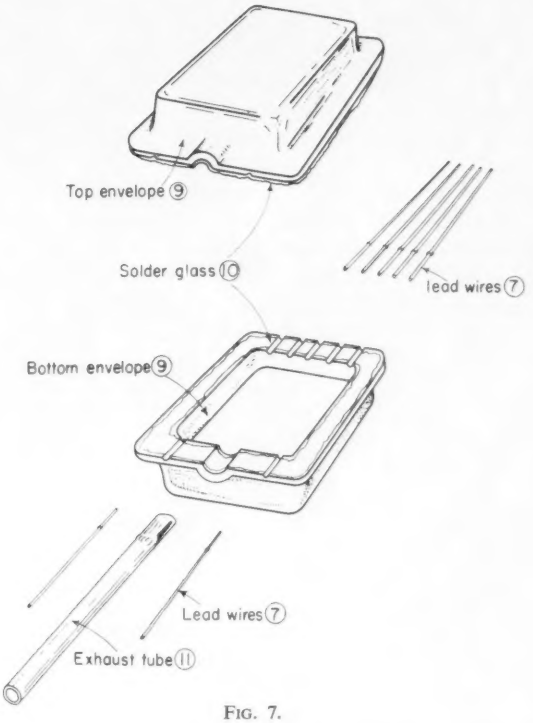

FIG. 7.

$\frac{1}{4}$ in. long sealed to a longer piece of No. 1720 glass tubing, both tubes have an outside diameter of $\frac{1}{8}$ in. The lead wires are made of two pieces, tungsten through the seal area and low carbon nickel on the outside of the envelope; the diameter of the leads is 25 mils.

Processing with solder glass code 7574

The application of this newly developed solder glass to the surfaces to be joined is by mixing the glass granules with binder of nitrocellulose to the consistency of a paste. This mixture is applied to the flanges, approximately 20 mils thick. The short piece of the exhaust tubulation is also coated with the solder glass mixture. After preliminary drying the envelopes and exhaust tubulations are pre-glazed in an air atmosphere at 620°C; also the lead wires are pre-glazed in the same manner, on that portion of the lead which passes through the flanges.

Hereafter all parts are loaded in a fixture for sealing. This is done in a nitrogen atmosphere at 720°C for 60 min. The heating and cooling rate during this process should be maintained to 3° per minute. Since the solder glass is a thermosetting glass the degree of crystallization is a direct function of time and temperature. Each crystallite acts as a center for further crystal growth as the heating continues and during this time some of the properties of the material change; for instance the coefficient of linear expansion decreases.

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Lead wire protection

To protect the lead wires against oxidation during processing and later operation at high ambient temperature it was found necessary to coat the tungsten part with gold. Considerable care must be taken in obtaining this protective gold plating. At first the lead is ultrasonically cleaned and electropolished. Then a gold strike is applied, which is then sintered onto the tungsten surface. Hereafter the actual gold plating is done for about 10 min and again sintered at 800°C for 10 min in a protective atmosphere. As the last step the lead portion, passing through the seal area, is then coated with solder glass and pre-glazed at 620°C for 5 min (as previously outlined under processing with solder glass).

The above process yields a gold layer of 0.1 to 0.4 mil in thickness. Platinum and rhodium might be possible substitutes for gold, but have not been investigated.

Envelope evacuation

After sealing, the exhaust tubulation is provided with an additional length of glass tubing (also No. 1720) of larger diameter, which contains standard barium-aluminum getters ; see Fig. 8. This larger tubing is connected to the pump and the body proper is enclosed in an electric oven. Evacuation takes place at 750°C and after tipping-off the larger tube the getter is flashed. Getter flash is mainly used to serve as a visual indicator of the condition of vacuum in subsequent testing.*

Summary of final tests

The various tests made on envelopes are shown in the following table, Fig. 9. The results obtained demonstrate that Pyroceram No. 9606 is a satisfactory material for electronic devices, operating at high ambient temperature.

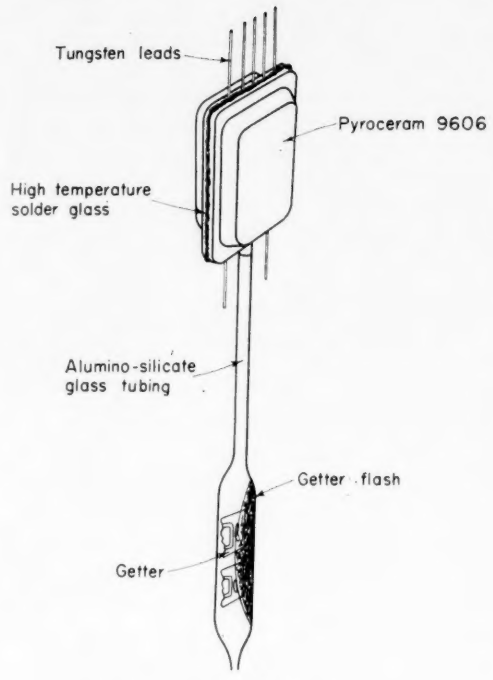

FIG. 8.

The process of manufacture of this material will assure homogeneity and uniformity of characteristics. Its advantage is the fact that it can be fabricated into various shapes by well known mass production techniques and is composed of non-strategic materials. The permeability to gases at elevated temperature is superior to most glasses and about equal to the high purity aluminum oxide ceramics. Electrical characteristics are good for most applications. Volume

Permeability : To Helium : At 500°C equal to No. 7740. At 300°C.
To Air : At 500°C $K = 4 \times 10^{-13}$ vs. $K = 6 \times 10^{-14}$ For No. 7740 at 300°C.

	Specimens Tested	Duration of Test	Test Condition	Result
Shelf Life	9	5000 hr	H.F. Coil, getter observation	No failures
Salt Spray	4	100 hr	Mil Std. 202 Method 101	No corrosive effects
Radiation Exposure	2	282 hr	7×10^{-18} NVT	1 gassy, no failures for vacuum
d.c. Resistance	3	0 hr	500°C, 250 V, 0.135 in. spaced leads	~ 125 megohms
Moisture Resistance	10	10 days	Mil Std. 202 Method 106	9-O.K., 1 failure for vacuum
Thermal Shock	14	2 min 15 sec	Acetone, from 23°C to −76°C Water, 0° to 100° to 0°C	No failures No failures
Thermal Cycling	13	45 min	Heating, to 750°C at 40°/min Cooling, from 750°C to 200°C at 20°/min	No failures No failures
Life at 500°C Life at 400°C	5 5	1508 hr 5684 hr	Continuous exposure to 500°C Continuous exposure to 400°C	3-O.K., 2 failures at 1409 hr No failures

FIG. 9. Tests made with evacuated, Pyroceram Code 9606 envelopes having seven leads.

*Actual construction of electron devices will make it necessary to place suitable getter material inside the envelope.

resistance is less at elevated temperature than alumina ceramics. The mechanical properties of the material are sufficient for most applications in the tube field. Due to its comparatively low coefficient of expansion and mechanical strength (up to four times that of glass) it can sustain large temperature gradients and exhibits good thermal shock properties. It is compatible for use with the refractory metals. Tungsten leads up to 0.030 in. *dia.* have been found to make satisfactory seals throughout the temperature range with Pyroceram Code 9606. Molybdenum should also be applicable in some products, its poor resistance to oxidation is a limiting factor.

Chemically the material contains no elements in sufficient quantities which could be considered harmful and it is stable when exposed to gases and chemicals. Resistance to radiation also can be considered satisfactory at intensities up to 10^{18} nvt.

Experimental envelopes made of Pyroceram Code 9606, solder glass and tungsten nickel lead wires have given satisfactory peformance of 1000 hours at 500°C and many more hours at 400°C.

Acknowledgment

The authors are indebted to the Corning Glass Works Research Laboratory for their advice and cooperation.

At the Westinghouse Tube Division Laboratory H. Heyn made many contributions to the sealing techniques, K. Rohrer to the plating of lead wires and C. Spangenberg obtained the data for permeability.

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The Use of Aluminosilicate Glasses in Experimental Vacuum Devices

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Introduction

Conventional glasses are particularly well suited for use as envelopes for vacuum devices because they can easily be shaped and electrical leads can be sealed through with little difficulty. Their transparency permits visual observation and relatively good dissipation of radiation. The most serious drawback of these glasses is that they soften at temperatures below 500°C; temperatures higher than this are often important, particularly for tubes to be operated at high ambient temperatures. Low temperatures on exhaust limit the ultimate vacuum obtainable[1], and this has led, in part, to the investigation and use of other envelope materials including ceramics, silica and aluminosilicate glasses.

The ability of ceramics to withstand high temperatures seemingly solves this shortcoming[2]. However, ceramics impose their own limitations, particularly for experimental work. For example, ceramics cannot readily be shaped but must be obtained in the desired form from the supplier. They are opaque. Ceramic-metal seals are difficult to make and are less flexible in design than glass-metal seals. Moreover, there is always the possibility of unwanted deposits being formed due to sublimation during sealing. Most seals require the use of protective atmospheres during bakeout to prevent oxidation and subsequent failure. Also, some metal-ceramic assemblies are quite permeable to gases at elevated temperatures, thus limiting bakeout temperature.

The use of fused silica or high-silica glasses affords another means of overcoming the temperature limitations of conventional glasses. Here, however, the very low coefficient of thermal expansion limits the size and shape of the seals that can be made to metals. In addition, the high temperatures (1700–1800°) necessary to work high-silica materials are another drawback to their use.

Recently a number of aluminosilicate glasses have been made available commercially. These glasses are of marked interest in that they can withstand bakeout temperatures in excess of 600° and can be worked by conventional glass-blowing methods when a suitable oxidation-resistant sealing metal is employed.

Protective atmospheres and bell-jar techniques for making the necessary seals using either pyroceram frits[3] or glass-melting techniques[4, 5] can also be used. However, these methods are cumbersome, and if the resulting seals are to withstand high-temperature bakeout in air, oxidation-resistant sealing metals must be used.

Experimental work in Bayside

Flame-working of the aluminosilicate glasses is more difficult than that of conventional glasses because working temperatures are considerably higher and because these glasses tend to reboil or bubble due to the release of gases near the surface. Reboil can be minimized or eliminated by sealing in a reducing flame, or by bubbling the heating gas through a suitable material such as a 5 per cent solution of methyl borate in methyl alcohol, or ethyl orthosilicate through which a specific small part of the gas is bubbled[6]. In the latter case the proportion of gas supply passing through the organic silicate is rather critical.

We have simplified the gas supply problem for small seals, say up to 1 in. *dia.*, by passing all the gas over an ethyl-orthosilicate-saturated wick. For tubing larger than 1 in. the wick is omitted, and with tubing larger than 2 in. the organic silicate is cooled in an ice bath to prevent the pick up of an excessive amount of silicate; excess silicate deposits on the cold zones and leaves the surface cloudy.

Another difficulty in working the aluminosilicate glasses is that the metals to which they seal, molybdenum and tungsten, oxidize readily at relatively low temperatures. These oxides are poorly adherent to the parent metal, non-protective to further oxidation, and volatile at sealing temperatures. For these reasons we were led to investigate the possibility of pretreating the sealing metal to form a suitable protective film on its surface. At elevated working temperatures tungsten embrittles rapidly. Molybdenum is less susceptible to embrittlement and is therefore the sealing metal chosen. Electroplating has been tried using chromium, nickel and other metals, but is too unreliable to be practicable. The use of a silicide coating[7, 8] for protecting molybdenum against oxidation has been suggested, but our experience indicates that extreme measures must be taken to avoid failure of such seals.

We have had excellent results using "Chromallized" molybdenum. Chromallizing* is a vapor-phase method of depositing a dense layer of chromium on molybdenum or other suitable substrate. At the high temperatures employed in Chromallizing, diffusion occurs between the metals to form a case. In general, the case structure developed contains a high chromium content near the surface, grading to pure molybdenum below. The bond developed between the case and the core is extremely adherent and the graded chromium content minimizes thermal expansion problems.

Oxidizing the surface chromium in wet hydrogen at 1100° for 10–15 min imparts adequate oxidation resistance; the oxidized surface can withstand not only direct flame sealing at 1200–1300°, but also annealing and extended high-temperature bakeout.

*Chromalloy Corporation, West Nyack, New York.

Another solution to the flame-working problem lies in using oxidation-resistant alloys and a Houskeeper-type seal. This permits the successful joining of metals and glasses having different thermal coefficients of expansion. We use Sylvania No. 4 alloy because its chromium content makes it one of the most oxidation-resistant of the glass sealing alloys.

This alloy readily withstands the high temperatures required for working aluminosilicate glasses. Experimental devices have been constructed using Sylvania No. 4 alloy Houskeeper seals and Chromallized molybdenum pins with Corning 1720 glass.

The bulb seals are 2 in. *dia.* and the stem seal is $1\frac{1}{2}$ in. The No. 4 alloy was spun into the appropriate form from 0.050 in. sheet. After machining, the parts were fired at 1100° in wet hydrogen for 4 hr to oxidize the surface chromium. The thickness at the feather edge should be one mil or less ; a $\frac{1}{4}$ in. back the thickness is 6.0 mils ; these dimensions are about half those of a copper Houskeeper seal. The No. 4 alloy parts are glassed with precut lengths of tubing, using inside-outside seals and annealed in an air furnace at 715° for 15 min.

The 0.060 in. molybdenum pins are cut to size, fired first in dry hydrogen and then under vacuum at 950°C. After Chromallizing, the pins are cleaned and again vacuum fired to remove any remaining volatile matter ; this may be important in view of the fact that halides are used in the Chromallizing process. After oxidizing they are glassed with 1720 beads. The button stems are made from 1720 glass cups blown into a graphite mold shaped with recesses for pins and tubulations. After annealing, the protrusions left by the recesses are removed with a glass-cutting wheel for pin and tubulation insertion. The cups are cleaned with concentrated hydrofluoric acid, preheated to 650° in a muffle furnace, and transferred to a heated jig ; the pins and tubulations are then fired in place with a hand torch. After completion they are transferred while hot to the muffle furnace and annealed in air at 715°.

Final tube closure is done by heliarc welding the edges of the telescoping stem flange to that of the tube envelope in order to minimize any possibility of contaminating the tube parts. The tubes are sealed to the vacuum system with a graded glass seal from Pyrex to Cobalt glass to uranium glass to 1720. The vacuum system used can readily attain pressures of 5×10^{-9} mm or better with adequate bakeout. However, since pressure readings during bakeout are important, it was necessary to rearrange the ovens so that the ion gauge was not baked, and this degraded the vacuum to 4×10^{-7} mm.

Tubes are baked out in air at 625° for 20 hr. This temperature is reached in about 1 hr. A maximum evolution of gas is observed at 500°. The system pressure with the tube hot after the twenty-hour bakeout was 5×10^{-7} mm and did not change after tip off, strongly indicating that these seals are not permeable to air at elevated temperatures.

Careful inspection showed no obvious damage to either the Houskeeper or pin seals ; some red iron oxide is seen. The tubes are easy to process because most of the gas is removed during bakeout.

The methods described can be employed to construct heat-resisting vacuum tubes using conventional glassblowing methods. The superior high-temperature properties of the aluminosilicate glasses permits both better vacuum processing and higher operating temperatures.

We wish to acknowledge assistance of John D'Angelo in this work.

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How Vacuum Tube Problems are Solved by the Use of Radioisotopes

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Introduction

Radioisotopes are atoms that give off radiations. Because these isotopes are detectable, measurable and discrete, can pass through materials, and can alter the properties of materials placed within range of their radiations, they represent an extremely valuable diagnostic tool.

Industry in general* and the electronics industry in particular was quick to recognize the value of radioisotopes in solving problems relating to manufacturing processes, product analysis, and research. Specific uses of the radiotracer technique for example, include determination of the rate of diffusion of materials in semiconductors, metals, and glasses ; determination of the presence of impurities in semiconductors ; determination of the rate of wear of tool tips in punch-press operations ; study of migration of cesium in photosensitive surfaces of television camera tubes ; evaluation of the cleaning power of etchants for printed-circuit boards ; and study of diffusion of nickel in fluorescent-lamp components.

Electron-tube studies

Radioisotopes and radiotracer techniques have been successfully used to attack and solve specific problems directly associated with the design and manufacture of vacuum tubes.

Such processes as water rinsing of etchants from cathodes, trichloroethylene degreasing of stainless-steel gun parts, and bake-out operations of organic materials have been investigated by the radiotracer technique.

In addition, radiotracer techniques have been used to solve problems of equipment design ; for example, studies have indicated methods for minimizing backstreaming in oil diffusion pumps and have established a test comparing the performance of ultrasonic cleaning equipment.

Finally, certain materials used in vacuum tubes were evaluated by radiotracer studies, for example, the absorption and retention of carbon dioxide by graphite coatings, the thermal decomposition of organic materials such as polyvinyl alcohol and ethylene glycol, and the sources of carbonaceous gases and other impurities of cathode nickel.

Rinsing of acid residue from cathode sleeves

One of the processes used for cleaning nickel cathode sleeves includes an acid treatment in a mixture of acetic and nitric acids. A radiotracer study was designed to determine how efficiently the etchant was rinsed from the cathode sleeves. Samples of cathodes were treated with acetic acid labelled with carbon 14, and were then processed by the various rinsing procedures under study. The radioactivity remaining after rinsing was measured as an index of residual acid.

Figure 1 shows the procedures involved in the preparation of the parts for contamination and subsequent measurement for residue. A small quantity of radioactive acid is heated

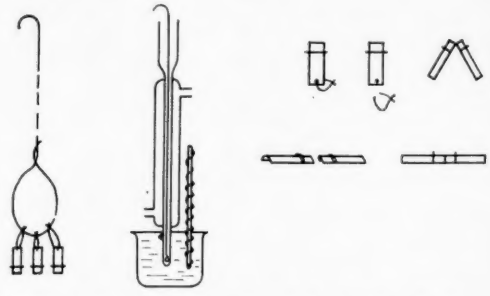

FIG. 1. Equipment and procedure used in testing effectiveness of various rinsing techniques.

by immersion in boiling water, and the cathodes are then lowered into the etchant by means of a nickel wire. After being rinsed, the cathode cups are cut so as to provide accurate measurement of residue on both the inside and outside of the part. The results of the study are shown in Table I.

TABLE I

The effectiveness of various rinsing techniques

Process	Monolayers	Ratio Inside — Outside
Standard	25.6	6.66
Ultrasonic, cold	0.68	2.47
Ultrasonic, hot	0.09	2.13
Hot	0.86	6.54
		per cent Residual contamination after firing
Hydrogen firing	0.40	2.0
Air firing	0.009	0.03

Degreasing with trichloroethylene

Trichloroethylene degreasing of metal parts is a process extensively used in the electron-tube industry. Lubricants and drawing compounds used in the formation of electron-gun parts, for example, must be completely removed from each part before it is put into service. The effectiveness of

*The National Industrial Conference Board, 460 Park Avenue, New York 22, N.Y., has surveyed industry in general, and has prepared its findings in a publication entitled, " Radioisotopes in Industry ".

trichloroethylene degreasing was determined by the removal of radioactive stearic acid from stainless steel. The stearic acid contaminant was labelled with carbon 14 at the carboxyl carbon. As shown in Fig. 2 an effective liquid-phase

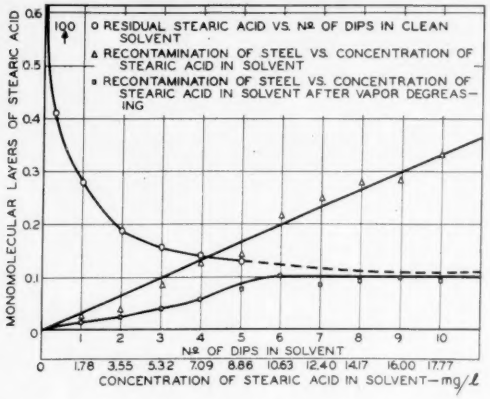
o RESIDUAL STEARIC ACID VS. Nº OF DIPS IN CLEAN SOLVENT
Δ RECONTAMINATION OF STEEL VS. CONCENTRATION OF STEARIC ACID IN SOLVENT
o RECONTAMINATION OF STEEL VS. CONCENTRATION OF STEARIC ACID IN SOLVENT AFTER VAPOR DEGREASING
100
MONOMOLECULAR LAYERS OF STEARIC ACID
0.6
0.5
0.4
0.3
0.2
0.1
0
1 2 3 4 5 6 7 8 9 10
Nº OF DIPS IN SOLVENT
0 1.78 3.55 5.32 7.09 8.86 10.63 12.40 14.17 16.00 17.77
CONCENTRATION OF STEARIC ACID IN SOLVENT—mg/l

FIG. 2. Results of trichloroethylene degreasing study. Each dip represents a 3 min submersion.

degreasing operation involving three 3 min dips in boiling trichloroethylene results in a residue closely approaching 0.1 monomolecular layer. Although not so effective as liquid-phase degreasing, vapor degreasing is valuable in that it minimizes recontamination of the parts from a dirty solvent.

Improvement in the design of diffusion pumps as related to oil backstreaming

The high-vacuum capabilities of oil diffusion pumps are at times reduced by the problem of diffusion oil backstreaming. Backstreaming, however, can be minimized by the use of properly designed auxiliary equipment about the pump. Various designs for baffles and "stack coolers" were evaluated by measurement of the amount of radioactive oil from the pump entering a vacuum tube being exhausted. Di-(2-ethylhexyl) sebacate, commonly called "Octoil S", was labeled with carbon 14 and used in a conventional MCF-60 pump. Table II indicates the extreme sensitivity of the radiotracer technique, in that conventional methods such as ether extraction or chemical analysis would not indicate accurately 5μg of backstreaming oil let alone 0.1μg of oil.

TABLE II

Results of oil-backstreaming study

Condition	Backstreaming of Diffusion-Pump Oil	
	Total Oil, μg	per cent Eliminated
No Stack Cooler, no Baffle	5.2	0
Coil Stack Cooler, no Baffle	3.1	40
Improved Stack Cooler, no Baffle	1.4	73
No Stack Cooler, Standard Baffle	1.8	65
No Stack Cooler, Improved Baffle	1.0	80
Coil Stack Cooler, Standard Baffle	0.8	85
Coil Stack Cooler, Improved Baffle	0.3	94
Improved Stack Cooler, Standard Baffle	0.4	92
Improved Stack Cooler, Improved Baffle	0.1	98

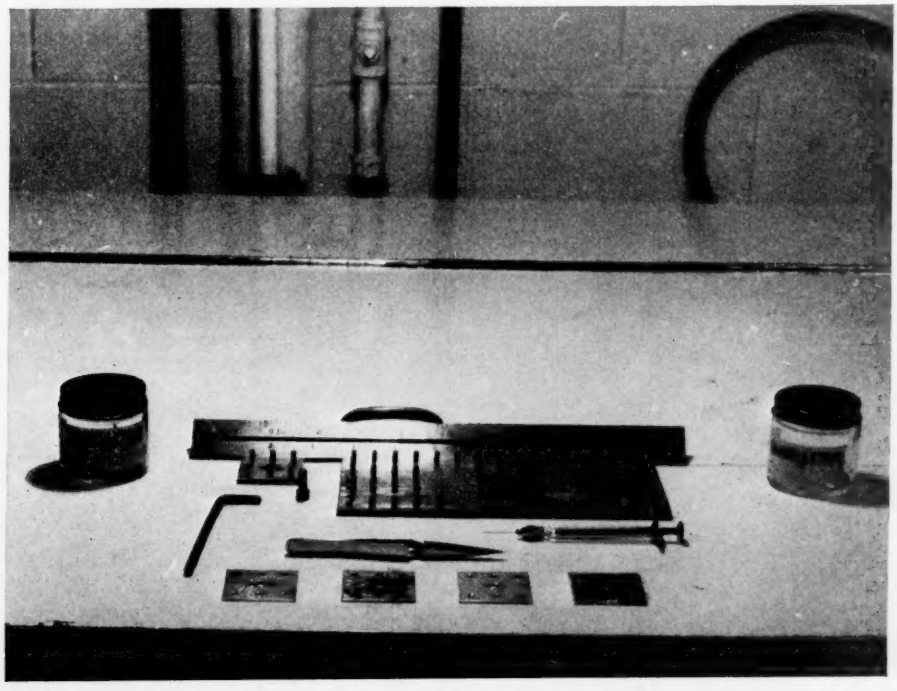

FIG. 3. Equipment used to label and clean deep-drawn cathode cups for the evaluation of ultrasonic cleaning equipment.

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Evaluation of ultrasonic cleaning equipment

The ability of ultrasonic cleaning equipment to remove radioactive grease from a television picture-tube cathode was studied by means of a technique in which radioactive stearic acid was applied to the insides of deep-drawn cathode cups. The degree of soil removal was measured after the labeled parts were cleaned in a detergent solution by means of ultrasonic cavitation. Effectiveness of degreasing was studied as a function of the following factors : (a) the addition of ultrasonic energy, (b) the load of parts being cleaned, (c) the de-aeration of the load being cleaned, (d) the size of the ultrasonic equipment, (e) the frequency of the ultrasonic equipment, and (f) the input power of the ultrasonic equipment. As a result of this study, a meaningful test and test apparatus were designed for the measurement of the degreasing potential of any ultrasonic cleaning device. Figure 3 shows the equipment used to contaminate and prepare the cathode cups for ultrasonic cleaning and Figs. 4 and 5 indicate some of the results of this work.

Absorption and retention of carbon dioxide by coatings

The radiotracer technique was found to be applicable to the study of the absorption and retention of CO_2 by graphite coatings. Graphite-silicate coating systems were exposed to CO_2 prepared from $BaCO_3$ labeled with C^{14}. This study showed that the absorption and retention of CO_2 by graphite coatings increases exponentially as the alkaline content of the coating increases, and as the surface area of the graphite increases. Figure 6 shows the apparatus used to prepare the radioactive carbon dioxide and expose samples of coating to the gas. Figure 7 shows the relocation of the radioactive gas from the labeled coating to other portions of a color tube as a result of electron bombardment.

Thermal decomposition and pyrolysis of organic material

The assurance of complete bake-out and removal of organic binders and reagents used internally in vacuum tubes is an ever-present problem. Several problems of this nature were resolved by the use of radioisotopes. A radiotracer study, for example, was performed to determine how

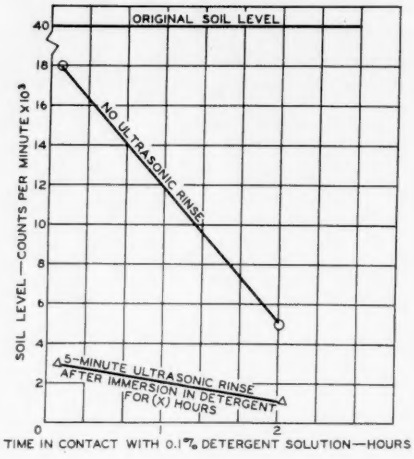
ORIGINAL SOIL LEVEL
NO ULTRASONIC RINSE
5-MINUTE ULTRASONIC RINSE AFTER IMMERSION IN DETERGENT FOR (X) HOURS
SOIL LEVEL—COUNTS PER MINUTE x10³
TIME IN CONTACT WITH 0.1% DETERGENT SOLUTION—HOURS

FIG. 4. Effectiveness of soil removal in detergent solution with and without ultrasonic cavitation.

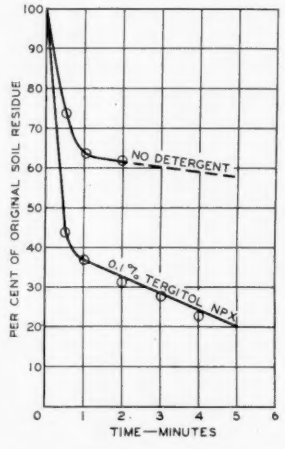

FIG. 5. The influence of detergent on ultrasonic cleaning.

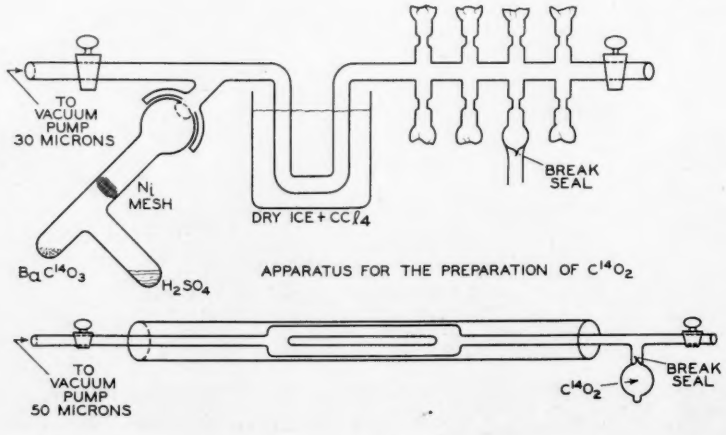

FIG. 6. Apparatus used for the preparation of $C^{14}O_2$ and exposure of samples.

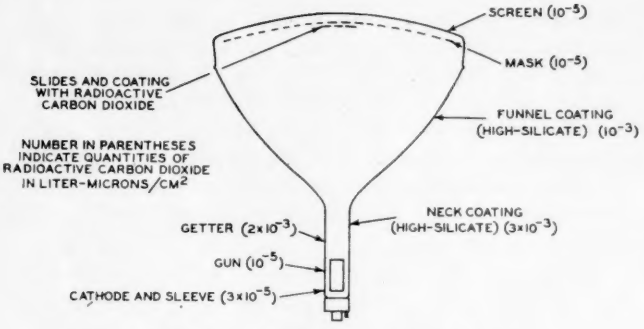
SCREEN (10^{-5})
MASK (10^{-5})
SLIDES AND COATING WITH RADIOACTIVE CARBON DIOXIDE
FUNNEL COATING (HIGH-SILICATE) (10^{-3})
NUMBER IN PARENTHESES INDICATE QUANTITIES OF RADIOACTIVE CARBON DIOXIDE IN LITER-MICRONS/CM²
NECK COATING (HIGH-SILICATE) (3×10^{-3})
GETTER (2×10^{-3})
GUN (10^{-5})
CATHODE AND SLEEVE (3×10^{-5})

FIG. 7. Distribution of CO_2 in a color tube.

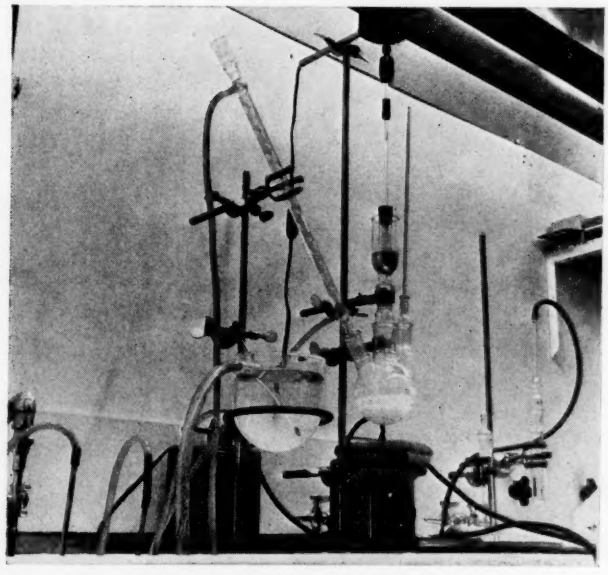

FIG. 8. Apparatus used to polymerize vinyl acetate.

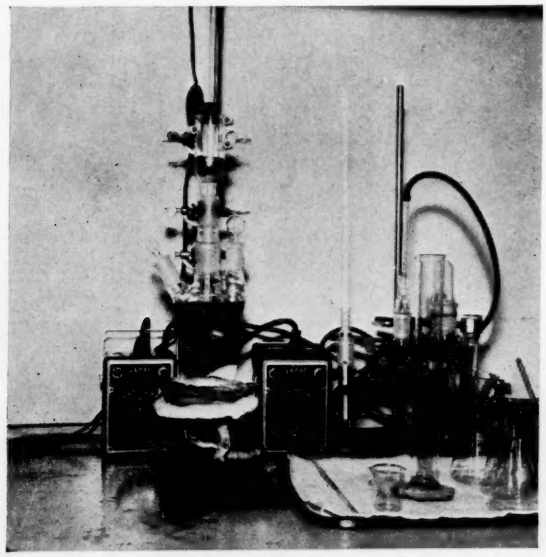

FIG. 9. Apparatus used to hydrolize polyvinyl acetate to polyvinyl alcohol.

the residue from polyvinyl alcohol varied as a function of process time and temperature. Polyvinyl alcohol is an organic material used to bind phosphors to the inside surface of a television picture tube. A feature of this work was the synthesis of the radioactive form of polyvinyl alcohol from vinyl acetate. Figure 8 shows the apparatus used to polymerize vinyl acetate to polyvinyl acetate, and Figure 9 shows the apparatus used to hydrolize polyvinyl acetate to polyvinyl alcohol (PVA). Figures 8 and 9 also show some of the safety precautions taken to minimize the spread of radioactivity.

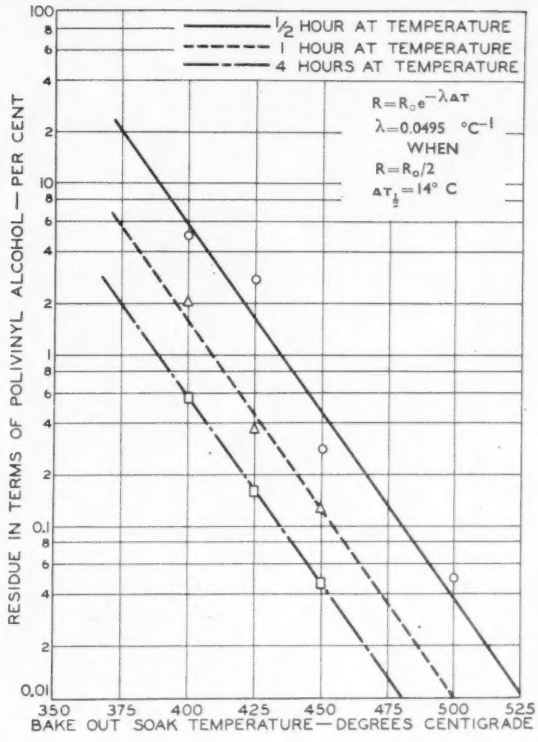

FIG. 10. Results of the pyrolysis of polyvinyl alcohol.

As shown in Fig. 10, the percentage residue in terms of PVA decreases exponentially with increasing temperature, following the equation $R = R_0\exp(-0.0495T)$ where R_0 and R are residues of PVA initially and at temperature T (°C), respectively. This equation indicates that a 50 per cent decrease in PVA residue results from a temperature increase of 14°C. Chemical kinetic treatment of the data also disclosed that the dominant reaction taking place below 5 per cent residue of PVA was the second-order heterogeneous reaction $C + \frac{1}{2}O_2 \rightarrow CO$. Radioactive PVA was also used to evaluate the bake-out operation of the color picture tube for possible process change. Table III lists the relative carbonaceous residues remaining in a color tube as a result of eliminating the first bake-out operation of the panel.

The completeness of the removal of ethylene glycol used in color-tube screen application was also evaluated by means of the radiotracer technique. Screens prepared with radioactive ethylene glycol indicated no ethylene glycol remaining after the photographic processing of the screen (screen

TABLE III

Polyvinyl alcohol residue as a function of tube processing

Presence of PVA Residue on :	Activity due to Standard Processing (with screen bake), counts/min	Activity due to Process Change (without screen bake), counts/min
Screen initially	12,250	11,000
Screen after aluminizing	10,300	8,000
Screen after screen bake	0	—
Screen after seal bake	0	0
Screen after exhausting	0	0
Funnel coating after seal bake	5	62
Funnel coating after exhausting process	10	14
Shadow mask	0	0

development). Three screens prepared with 3 to 4 times the normal quantity of ethylene glycol showed 0.5 per cent carbonaceous residue after screen development. The samples showed no carbonaceous residue after screen bake when tested by conventional counting methods. However, when the phosphor was removed from one of these tubes and tested by means of an extremely sensitive proportional-counting technique, 0.025μg of residual ethylene glycol were found.

Determination of the sources of carbonaceous gases from nickel

When nickel strip used in the cathode of electron tubes is heated carbonaceous gases are evolved. Two sources of the carbon dioxide and carbon monoxide have been postulated ; the carbon contamination present on or worked into the metal surface, and the dissolved carbon normally present in nickel. The objective of the radiotracer work described here was to develop a technique to study the evolution of the

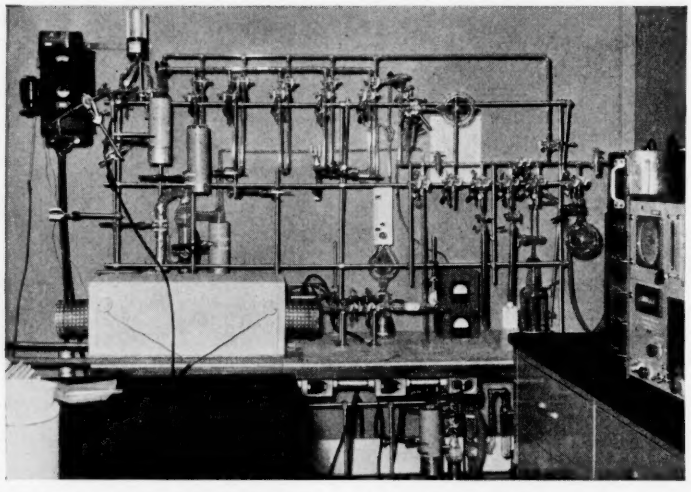

FIG. 11. Apparatus used to collect and measure radioactive $C^{14}O_2$.

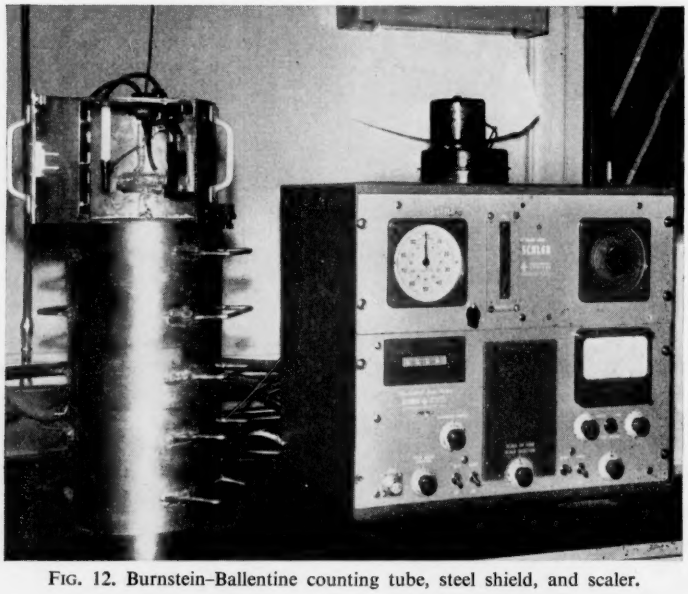

FIG. 12. Burnstein–Ballentine counting tube, steel shield, and scaler.

carbonaceous gases from nickel as it is related to each of these sources of carbon, and to study the evolution of carbonaceous gases from nickel as a function of processing*. Figure 11 shows the gas-collection apparatus designed and built to study the radioactive gases coming from nickel, and Fig. 12 shows the arrangement used to measure the radioactivity of the gas. It was necessary, of course, to prepare very pure nickel melts, in which carbon 14 was then dissolved. After this nickel was prepared into a 5 mil strip, identical samples were processed by degreasing and acid-etching techniques. Figures 13 and 14 show that for both processing techniques, the major portion of the evolved gases was radioactive ; i.e. gases originating from carbon dissolved in the nickel. Moreover, a comparison of the figures shows that the acid-etched sample exhibited a lower over-all gas evolution and a marked drop in non-radioactive gas ; i.e. gases originating from surface contamination. This observation supports the theory that oxides on the surface of the strip combine with diffusing carbon to evolve carbonaceous gases.

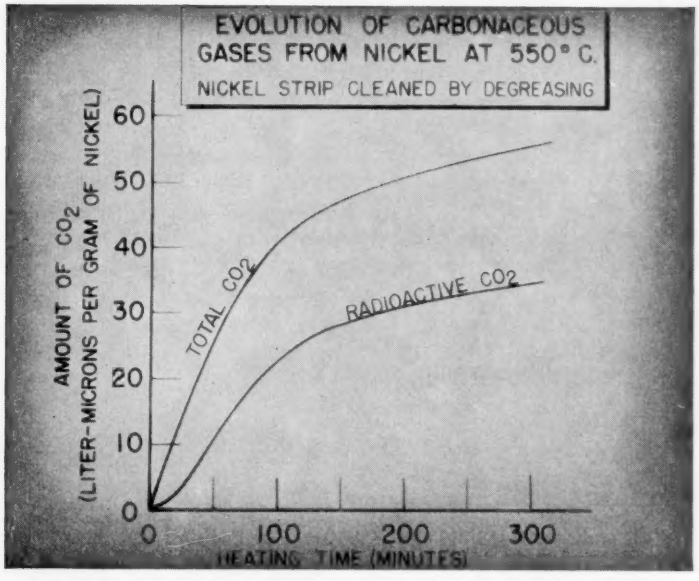

FIG. 13. Evolution of carbonaceous gases from nickel cleaned by degreasing technique.

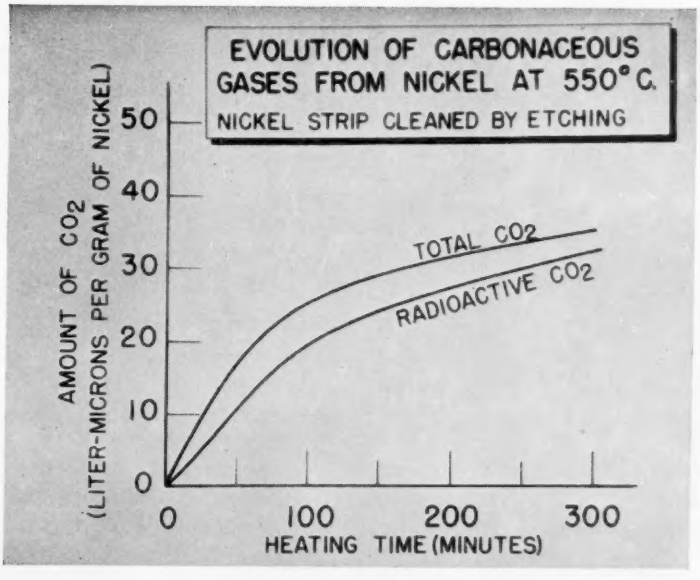

FIG. 14. Evolution of carbonaceous gases from nickel cleaned by etching technique.

*This work was supported by U.S. Army Signal Corps contract funds (Contract No. 36-039-sc-78226).

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FIG. 15. Radiotracer laboratory equipment.

Neutron-activation analysis

Neutron-activation analysis has also been employed to analyze tracer quantities of contamination on electron-gun parts. Sublimation products deposited on the third grid of the electron guns of tubes having good and poor emission after 5000 hr of operation were subjected to neutron analysis in an attempt to establish a correlation between emission " slump " and the sodium chloride constituent of the sublimation. As shown in Table IV, a definite correlation exists.

TABLE IV

Neutron activation analysis of sublimation on color picture tube grids

Condition of Tube after 5000 hr operation	Cl detected μg	Na detected μg
Cathodes showed signs of slump	1.2	1.20
Cathodes all showed good emission	0.7	0.26
Control (grid taken from new guns)	0.2	0.11

Counting apparatus

Figures 15 and 16 show the radiation-counting devices used in the work described. Pictured in Fig. 15 is the Baird Atomic Company's Multi-Scaler, Nuclear Measurements Corporation's Geiger-Mueller counting tube, Nuclear Measurements Corporation's windowless, gas-flow proportional counter, and a Baird Atomic Co. scintillation counter. Figure 16 shows a Baird Atomic Company Laboratory Geiger-Mueller rate meter.

Current studies

The following problems are currently under investigation or are being considered for investigation :

(1) The development of an optimum cleaning cycle for ceramic materials, and the study of the effect of low-level soils on ceramic-to-metal seals.

(2) The development of a method for measuring reducing agent of cathode nickel by the use of oxide cathode coatings prepared with strontium 89–85.

(3) A determination of the materials that become sources of gas under electron bombardment in vacuum tubes.

(4) The development of a method for measuring the rate of thoria evolution from thoriated tungsten, and the study of the evolution rate as a function of vacuum tube performance.

(5) The development of a method for measuring the permeation of gases through ceramic materials.

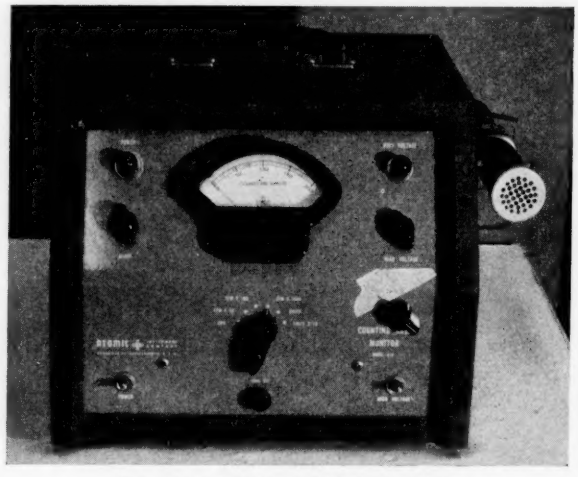

FIG. 16. Laboratory radiation monitor.

Conclusion

The examples cited in this paper have demonstrated the unique advantages of radioactive isotopes and the radiotracer technique. The ultra-high sensitivity of measurement by means of relatively simple techniques permits quantitative determination and location of complex materials related to the electron tube. Such advantages are realized in research savings and in the solution of problems hitherto insoluble.

Field Effects in Insulating Thin Film Secondary Emitters

H. J. BOLL

Vol. 11 1961

Introduction

The phenomenon of secondary electron emission has been studied at the University of Minnesota for a number of years. Our efforts have been directed toward gaining a basic understanding of the process itself and toward the attainment of high yields that are stable with time. Most of our experiments have been concerned with electrical insulators because of their higher yields.

In the applications of secondary emission it is often necessary that the secondary emitter be able to supply a steady current of secondary electrons. Because an insulating material of appreciable thickness cannot conduct a steady electrical current, the secondary emitter is usually made in the form of a very thin film on a metal backplate. The behavior of such films forms the subject of this paper.

Consider what happens when an insulating thin film is bombarded with primary electrons. Thinking in terms of the band model of solids, we say that the primary electron bombardment creates free carriers, holes in the valence band and electrons in the conduction band. If the insulating film is sufficiently thin, most of the free carriers can diffuse out of the film surface or to the metal backplate. However, no matter how thin the film, some of the free carriers will become trapped either at the surface of the film or in the bulk, and unless the densities of trapped electrons and holes are equal, the resulting space charge gives rise to an electric field within the film. This electric field can affect the escape probability of internal secondaries by either accelerating them toward the surface of the film or toward the backplate. For example, if the density of trapped holes is greater than that of electrons, the surface of the film becomes positive with respect to its metal backplate, and the electrons in the conduction band drift toward the surface where they can then escape from the film. In this case, the secondary yield is increased by virtue of the internal electric field. This increase is not to be confused with Malter effect where internal secondaries gain sufficient energy to excite other electrons from the valence band.

Another complication arises if there exist nonuniformities in the film structure or thickness. Such nonuniformities can result in a nonuniform potential distribution over the surface of the film, which in turn results in a so-called "coplanar grid effect". For example, consider a portion of the film surface that is charged more positively than the film surface surrounding it. Electrons emitted from this more positive portion experience a retarding field from the surrounding area. Hence, the lower-energy secondaries are returned to the film, reducing the apparent secondary yield. If these regions are relatively large in size, this effect may be overcome by applying a sufficiently positive collection potential but if they are microscopic in size, the required collection potential may not be attainable.

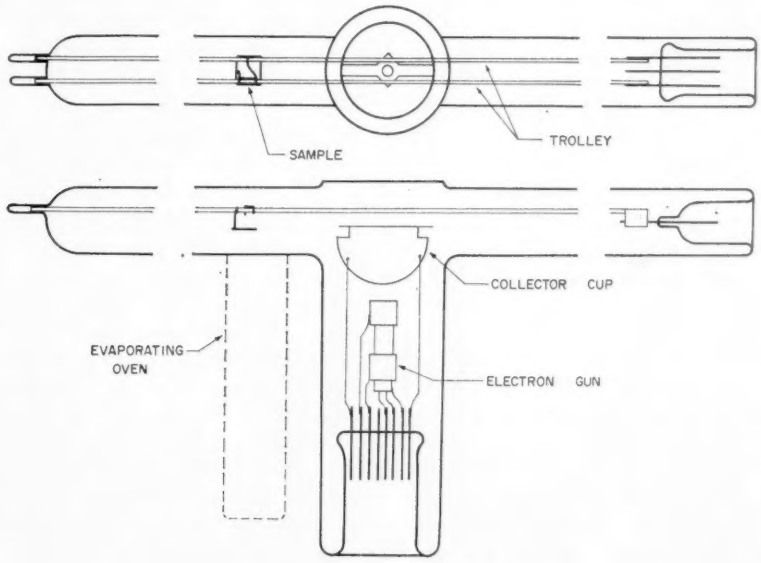

FIG. 1. Preparation tube.

Experimental techniques

The above mentioned effects have been studied in both MgO and Al_2O_3 films ranging from 100 to 1000 Å in thickness. The MgO films studied by K. L. Kliewer were formed on 1.7 per cent Mg–Ag alloy by heating in CO_2, and those that were studied by the author were formed on Pt, Mo, W, Ta, and Ti by first evaporating a layer of Mg onto the metal surface and then oxidizing this film by heating in oxygen. The Al_2O_3 films studied by Mr. J. Coburn and Mr. R. Nielsen were formed in a similar way on Mo by oxidizing an evaporated layer of Al and on Al by means of a standard anodizing technique.

A typical tube used for the experimental studies is shown in Fig. 1. The essential parts are the trolley on which the samples can be moved, an electron gun for a source of primary electrons and a hemispherical cup with a partially closed lid for collecting the secondary electrons. For those studies in which it is necessary, an evaporating oven for depositing Mg or Al onto the metal surfaces was attached to the side arm of the tube.

Experimental results

The experimental results with MgO films are described first, then the results with Al_2O_3.

MgO films

When a MgO film which has previously been electrically neutralized by heating in vacuum is bombarded with primary electrons and the secondaries are collected, it is observed that the secondary yield rises monotonically with time from an initial value to a somewhat higher steady-state value. This increase in yield is believed to be the result of the previously mentioned trapping of charge carriers within the film.

By way of illustration, let us consider the movement of the free charge carriers in some detail. A simplified drawing of the band structure in thermal equilibrium is shown in Fig. 2a. The primary electron bombardment creates electron hole pairs as shown in Fig. 2b. Electrons can either leave the film by emission from the surface or by diffusion to the backplate while the wholes can only leave via diffusion to the backplate. This being the case, under most circumstances, more holes will become trapped near the surface than electrons, causing the surface potential to rise positively as represented in Fig. 2c. As this occurs, electrons begin to drift toward the surface, and holes drift toward the backplate. This results in more electrons and fewer holes available for trapping at or near the surface of the film. The field increases in this way until a state of equilibrium is reached where the rate of hole trapping is equal to the rate of electron trapping. Since free carriers are produced at a finite rate, both the surface potential and the yield change at a finite rate. This rate is, of course, directly proportional to the primary current density.

It has been found that in general, the thicker films exhibit a greater fractional increase in yield due to the field. This is to be expected since at a high primary energy more internal secondaries are produced deep within the film and it is these which are affected most because the field can then exert its influence over a larger distance.

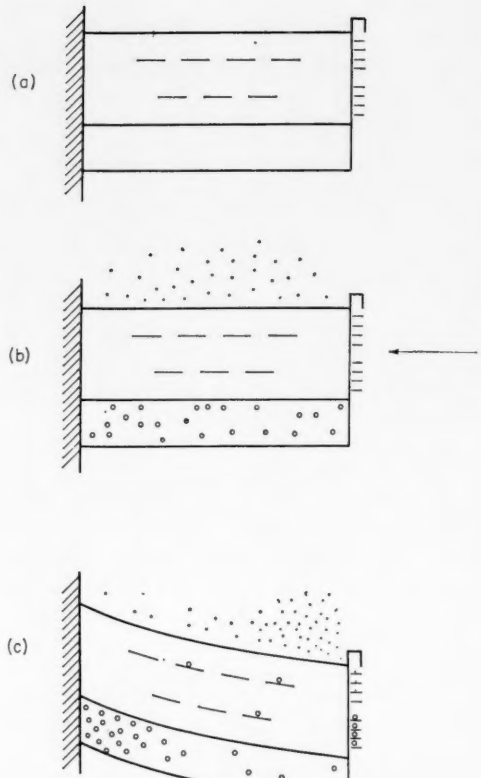

FIG. 2. Simplified diagram of band structure.
(a) Thermal equilibrium with empty trapping centers.
(b) and (c) Electron-hole configuration as a result of primary electron bombardment, before and after the trapping has occurred respectively.

If the primary electron bombardment is interrupted for a short time and then resumed, it is found that the secondary yield has not decreased from its previous higher value, indicating that the MgO film is a good electrical insulator. In order to obtain the lower yield again, the film must either be heated or bombarded with the collector-electrode-potential negative with respect to the film. In the latter case, the secondaries are returned to the film, thus making more electrons available for trapping. Experience shows that either of these two methods results in a yield approximately the same as the previous initial yield.

Subsequent to bombardment, the time required for a significant decrease to occur in the internal electric field at room temperature is different for different films, varying from a few seconds to many hours. In general, less time is required for the thicker films. The characteristics of all of these films are somewhat like a capacitance in parallel with a conductance that increases with increasing primary current density, increasing electric field, and increasing temperature. For example, at a constant primary current density, the positive potential at the surface of the film decreases with increasing temperature because the conductance of the film is increased. Hence, the increase in yield is less at higher temperatures. This result is shown in oscillogram of Fig. 3

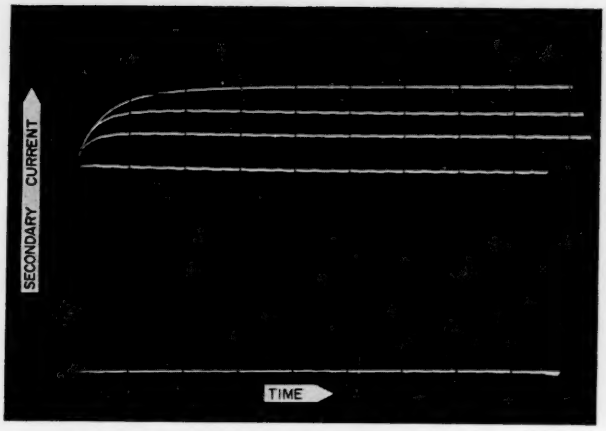

FIG. 3. Oscillogram of the rapid initial rise in secondary yield with temperature as a parameter. Traces in ascending order; base-line, $T = 400\,°C$, 300 °C,—150 °C and 25 °C.

where the lowest curve was obtained with the film at approximately 400 °C and the highest curve at room temperature. Thus, the yield of an insulating thin film may be a function of temperature indirectly through its internal electric field. The build-up of the internal field can be especially troublesome in pulse applications where the shape of the pulse may become distorted or the gain of the device may be a function of the pulse repetition rate.

In addition to the rapid initial increase in yield there are usually observed much slower long-term changes in yield during continuous electron bombardment. It is believed that these changes are either due to electron-bombardment desorption of a gas from the surface of the film, or due to the dissociation of the film itself. It has been observed that these long-term variations in some cases are solely the result of variations in the rapid initial increase in yield. That is, when bombardment induced changes in yield occur the initial yield of a discharged film before the build-up of the internal field does not change; only the magnitude of the rapid initial rise changes. This suggests that the long-term variations in yield are the result of variations of the internal field rather than variations in electron affinity. This result can be given some qualitative basis in the following way: if it is assumed that each surface atom of the MgO is a possible site for an adsorbed atom, then there can exist approximately 2×10^{15} adsorbed atoms per cm^2 on the surface. By way of illustration, let us assume that 0.1 per cent or 2×10^{12} of these are driven off by electron bombardment. Evidently this is too small a number to affect the electron affinity appreciably. If it is further assumed that each of the empty surface sites can trap an electron or a hole, then the above number represents a change in surface charge of $2 \times 10^{12} \times 1.6 \times 10^{-19} = 3.2 \times 10^{-7}$ coulomb/cm^2. Since the relative dielectric constant for MgO is approximately 10, the capacitance of the surface of the film 100 Å in thickness with respect to its backplate is,

$$C = \frac{0.0885 \times 10}{10^{-6}} \mu\mu\text{F/cm}^2 = 0.885\ \mu\text{F/cm}^2$$

Therefore, a charge of 3.2×10^{-7} coulombs residing on the surface of the film results in a potential $\Delta V = Q/C = 0.36$ V, which appearing across a film 10^{-6} cm thick represents a field $\Delta E = 0.36 \times 10^6$ V/cm. It will be shown later on in this presentation that this is sufficient to cause a significant change in yield. Thus, although a large fraction of a monolayer of foreign atoms must be desorbed from the surface to affect the yield via changes in electron affinity, it may be necessary to desorb only a very small fraction of a monolayer in order to affect the yield considerably via changes in the internal field.

The most direct evidence of an electric field within the MgO films is provided by the so-called collector characteristic curves, which are plots of secondary current as a function of the voltage between emitter and collector. The development of an oscillographic technique has made it possible to obtain these curves in an interval of time that is short compared to the time required for an appreciable change in internal electric field. Hence, the electric field is expected to change very little during the time in which the curves are traced. Oscillograms of two of these curves are shown in Fig. 4, where the arrows indicate the direction of traversal. In the upper curve, the yield has been raised to its higher value by means of a short period of primary electron bombardment with the collector positive. The collector potential is then swept rapidly from positive to negative to obtain the upper curve. Then the collector is held negative for a time sufficient to discharge the film. The next step is to trace the collector characteristic curve from negative toward positive collector potential. The horizontal shift between these two curves is a measure of the difference in surface potential in the two cases. Since this film was approximately 200 Å thick, this 2 V shift in Fig. 4 represents an internal electric field change of 10^6 V/cm. The rounded knee in the upper curve is believed to be the result of nonuniformities in the surface potential coupled with coplanar grid effect.

If these collector characteristic curves are traced very slowly so that the surface potential of the film can change appreciably during the trace, the oscillograms of Fig. 5 are obtained. Here, when the collector potential is changed from positive to negative, the usual curve is obtained. However, during the time in which the collector is negative, the secondaries cannot reach the collector and hence fall in a spray over the whole area of the film, discharging it. When the collector potential is slowly made positive, the potential of the bombarded region increases as more and more secondaries are able to reach the collector. However, the potential of the unbombarded region remains constant. When the potential of the bombarded region becomes more positive than the unbombarded region, the latter acts like a negative grid tending to return emitted secondaries to the bombarded region. This is the reason for the breakpoint in the return curve. The upper set of curves in Fig. 5 was obtained with a 2 mm *dia.* primary electron beam, and the lower one with a 4 mm *dia.* primary beam. Note the more pronounced effect in the former as one would expect.

Al_2O_3 films

With Al_2O_3 films, a rapid initial decrease in yield is observed instead of a rapid initial increase during primary

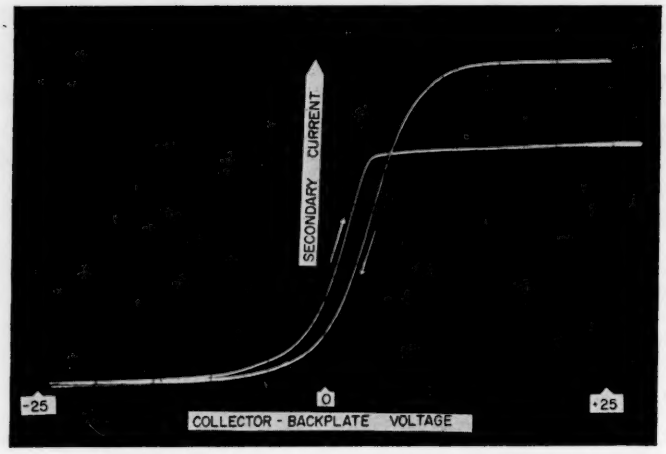

FIG. 4. Oscillogram of collector characteristic curves with a rapid horizontal sweep speed.

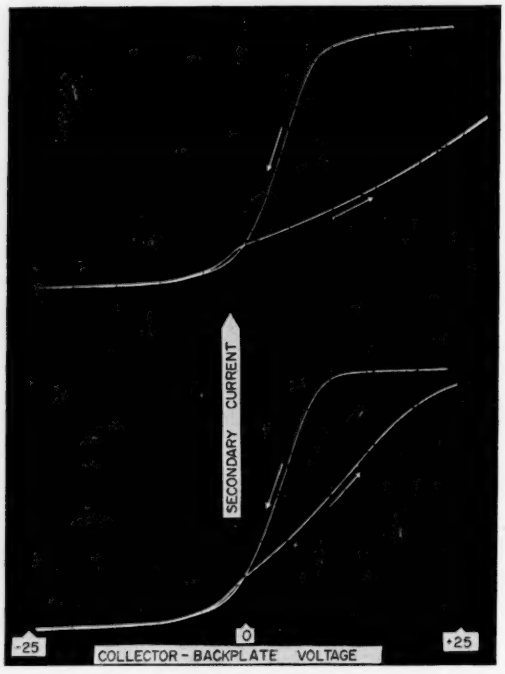

FIG. 5. Oscillograms of collector characteristic curves with a slow horizontal sweep speed. Top—with 2 mm ; Bottom—with a 4 mm diameter primary beam.

electron bombardment. The discussion above shows that this behavior may be the result of a charging of the film coupled with a coplanar grid effect tending to return secondaries to the film. This same behavior has also been observed with MgO in isolated cases where it was believed that the film was very nonuniform in thickness.

Collector curves similar to those of the MgO films are obtained with Al_2O_3 films except that the horizontal shift between the two collector characteristic curves is much greater than for MgO films indicating a much higher internal electric field in the former.

Summary

A horizontal shift in the collector characteristic curves suggests the presence of an electric field of 10^6 V/cm or greater within insulating thin film secondary emitters. This assumption is supported by the fact that changes in secondary yield occur corresponding to changes in internal field. Furthermore, effects have been observed which suggest that the structure of insulating films may be an important factor relating to their properties because of the coplanar grid effect.

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The Deactivation of Impregnated Type Cathodes Due to Metal Vapors

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Introduction

Thermionic cathodes used in microwave tubes are frequently affected by their environment. The use of metallic brazes and base metals in the construction of a microwave tube device, warrants a study of the poisoning effect of metal vapors on the emission properties of thermionic cathodes.

An investigation was therefore undertaken to determine the influence of various metal vapors on the impregnated-type cathode. Results are presented that indicate the influence of various metal vapors on the emission properties of thermionic cathodes as a function of metal vapor temperatures.

Method

An experimental diode was fabricated as shown in Fig. 1. The metal poisoning source (1) with its heater (2) was mounted

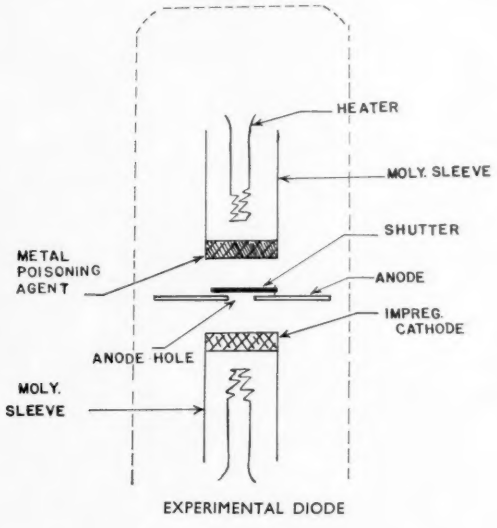

FIG. 1.

opposite an impregnated cathode (3), along with an intervening anode. There was a hole (5) in the anode and a moveable shutter (6) to allow for the direct evaporation of metal onto the cathode while drawing pulsed emission at the anode with ~2 kV on the anode.

The poisoning source usually consisted of a peened metal pellet (0.100 in. *dia.*) in a moly sleeve and was placed 0.050 in. from the anode hole (0.080 in. *dia.*) The cathode was mounted 0.025 in. away from the hole on the opposite side of the anode. The impregnated cathode consisted of a porous tungsten pellet (0.100 in. *dia.*) having 25 per cent porosity which was impregnated with a mixture of 3 mol BaO, 1 mol CaO, and 1 mol Al_2O_3. Brightness temperatures were measured with an optical pyrometer.

A standard Phillips type cold-cathode gauge was used for all pressure measurements during poisoning studies. Reliable performance has been obtained from the cold cathode gauge as a result of employing the same processing that should be used in outgassing any metallic components that are used in a vacuum system. The cold cathode gauge power supply was modified to measure small currents corresponding to pressures $\sim 1 \times 10^{-10}$ mmHg.

The processing of the system consisted of baking at 450°C overnight and induction heating of the anode in the experimental diode along with the elements of the cold cathode gauge. The cathode was activated in the usual manner, and the system was cold trapped and pumped to $\sim 1 \times 10^{-7}$ mmHg. The diode and pressure gauge assembly was then sealed off from the vacuum system, and the barium getter was flashed.

With the cathode in a stable activation state, temperature limited emission was drawn with the cathode at 1100°C_{Br} and a plate voltage of ~2 kV (rectangular pulses) having a repetition rate of 200 pulses/sec and pulse width of 1 μsec. The saturated current was measured by observing the voltage drop across a known plate resistor which was connected to an oscilloscope.

Prior to the poisoning run, the poisoning agent was further degassed with the shutter closed. Poisoning data were taken by recording the change in the temperature-limited emission while exposing the cathode at a fixed temperature to the poisoning agent. Poisoning data were usually taken under two conditions. A first set of data was taken with the poisoning agent sleeve electrically connected to the cathode sleeve. A second set of data was taken to observe electron bombardment effects. In this case the poisoning agent was electrically connected to the anode. During all observations of poisoning, the total pressure was $<10^{-7}$ mmHg. Recent work by the authors[1] indicates that only oxygen produces harmful effects on the impregnated cathode at these low pressures ($<10^{-7}$ mmHg).

A number of gas analyses of sample diodes used in the Raytheon Burlington Laboratory have been made using the

omegatron mass spectrometer. No partial pressures of oxygen were found to be present in the sample diodes for pressures near the limit of detectability (1×10^{-8} mmHg) of the omegatron that was used. Thus all poisoning diodes were processed and evacuated to rule out the possibility of oxygen poisoning or poisoning by any other gases during the observation of metal vapor poisoning. Observations of metal vapor poisoning were not begun until the effect of the hot poisoning agent on the cathode with the shutter closed was eliminated. In this manner, all poisoning data were taken to be metal vapor poisoning, due to line of sight evaporation onto the cathode.

Discussion and conclusions

The initial poisoning data were recorded by plotting the normalized saturated emission vs. time for several metal poisoning agent temperatures. A cathode temperature of 1100°C (brightness) was used in all poisoning studies and all poisoning agent temperatures were brightness temperatures. Figure 2 represents such a typical plot (nickel vapor poisoning). One can see that after ~10 min, the point of maximum cathode poisoning has taken place. Similar plots were made for all metals used in the poisoning studies. All metal vapors seemed to poison the cathode to a final I/I_0 value in 10 min, with the exception of copper. Copper produced no harmful effects on the cathode for copper temperatures up to the melting point of copper. Figure 3 represents a plot of the final I/I_0 value for all metals used vs. the operating temperature of the metal poisoning agent. The remaining metals poisoned the cathode to some extent, with the lower melting point metals usually poisoning the cathode at lower poisoning agent temperatures. Ag poisoned at the lowest temperature with Phosnic, Au, cupro-nickel, Ni, Ti, Fe, Pt and Zr following in that order. In all cases of poisoning, the cathode did not reactivate to its initial state in 10 min. Thus occasional hot shots were applied to the cathode in order to reactivate the cathode to its original activation state for subsequent

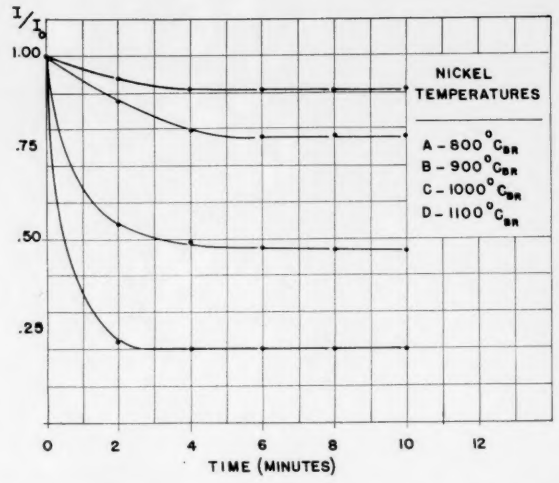

FIG. 2. Normalized saturated emission vs. time for an impregnated cathode (cathode temperature 1100°C_{Br}) in the case of nickel vapor acting on the cathode.

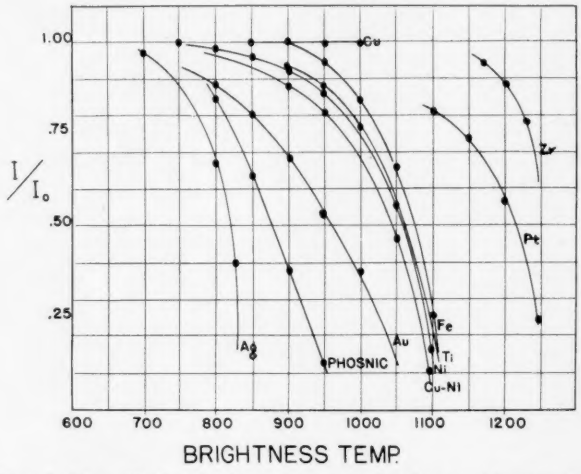

FIG. 3. Normalized poisoning current vs. poisoning agent temperature for various metals (cathode temperature −1100°C_{Br}).

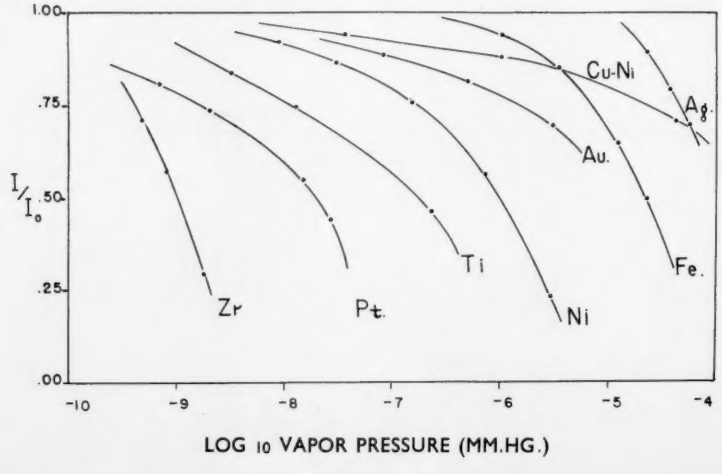

FIG. 4. Normalized poisoning current vs. poisoning agent vapor pressure for various metals (cathode temperature −1100°C_{Br}).

poisoning observations. Saturated cathode current densities were usually around 10 A/cm^2.

The mechanism of cathode deactivation due to metal vapors is not well understood. The story of what happens when an emitting surface is subjected to bombardment by hot metallic particles may involve the binding of some of the barium atoms to the metal particles, the alloying of the condensed metal with the tungsten matrix and other phenomena. Whatever the activity at the cathode, the action of the metal particles on the cathode emission would seem to be a function of the rate of arrival of these particles at the cathode and the number of these particles that arrive per second.

The particular geometry employed in the poisoning diodes does not allow one to use tabulated values of vapor pressure (to be found in the literature) as the true vapor pressures at the cathode. However a plot of I/I_0 (see Fig. 4) vs. vapor pressure (at poisoning agent surface) illustrates the trend of metal vapor poisoning for all the metals used in the studies. The plot was obtained by taking tabulated poisoning agent temperatures with their corresponding final values of I/I_0 from Fig. 3 and recording the corresponding vapor pressures from the literature. Hence a plot of I/I_0 vs. vapor pressure was made as shown in Fig. 4. Emissivity curves which had been previously obtained in this laboratory, allowed the conversion of poisoning agent temperatures in degrees brightness to °K. Figure 4 illustrates that, for a given vapor pressure, zirconium is the most harmful to the cathode, with silver being the least harmful. Copper and Phosnic were not included in Fig. 4 because copper did not poison the cathode and no data was available on the vapor pressure of Phosnic.

Electron bombardment of the poisoning agent during the poisoning observations produced no appreciable change in the poisoning vs. time curves for all the metals. With the exception of Cu–Ni, the poisoning curves of Fig. 4 demonstrate a definite trend and appear to form a family of poisoning vs. vapor pressure curves. The poisoning of the impregnated cathode by gold lends support to work done by J. A. Champion[2] in which gold evaporated in sufficient quantities on an oxide cathode poisoned the cathode within a relatively short period. Champion also observed that titanium seriously poisons an oxide cathode (by ~50 per cent) at a titanium temperature of 1100°C. His conclusion is that titanium reduces barium oxide to barium which in turn evaporates, thus depleting the effective emitting surface. X-ray analyses made in this laboratory indicated that titanium reacted with barium aluminate in the cathode thereby forming $BaTiO_3$ which is a poor electron emitter.

The data presented here on cupro-nickel is not conclusive since the true vapor pressure of cupro-nickel is not known. Most of the vapor pressure of cupro-nickel as obtained from the literature[3] is probably due to the vapor pressure of copper alone. The similarity in Ni and Cu–Ni poisoning of Fig. 3 and dissimilarity in Fig. 4 lends support to this argument.

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Acknowledgments

The authors wish to express their thanks to Mr. H. Homonoff who took some of the original data and to Mr. A. Amato for his assistance in the instrumentation and experimentation.

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Desorption of a Thorium Monolayer

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Introduction

The material to be presented in this paper pertains to that class of devices in which cathode emitters of relatively high temperature are used. This class includes microwave magnetrons and also more recently, those devices known as thermionic converters or plasma thermocouples which are designed for the conversion of heat into electricity.

A type of cathode which seems well adapted for these high temperature applications is that in which the emitting area is a refractory metal, usually tungsten, on whose surface some kind of monolayer is maintained for the purpose of reducing the work function.

Naturally the tube engineer is immediately interested in whatever circumstances may exist which might cause the removal or desorption of this monolayer film from the cathode surface. The two major causes of such desorption are of course, (1) bombardment of the film by one kind of particle or another, and (2) ordinary thermal evaporation of the film.

Recent studies at Bartol have been concerned with various aspects of the physics of the desorption of thorium atoms from a tungsten surface and some of these studies are here reported.

The major portion of this paper is concerned with thermal evaporation of a thorium layer. Brief reference will be made at the end to some previously unreported results concerning desorption by electron bombardment.

Evaporation measurements

In Fig. 1 is shown a tube which has yielded some results in both of these respects. It was designed primarily for studies of desorption by electron bombardment. In the course of those studies the evaporation data were taken which are here discussed.

In this tube a 10 mil tungsten filament about 3 in. long is mounted coaxially with three tungsten helices. The center one of these three serves as anode for measurement of thermionic emission from the filament, in which measurement the two adjoining helices serve as guard electrodes.

In the measurements having to do with desorption by electron bombardment which will be mentioned below, the helices are heated by passage of current and serve as sources of bombarding electrons. The filament and the helices are surrounded by a tantalum shield can which was intended to prevent bombardment of the glass by stray electrons with possible poisoning effects.

As shown in the diagram, a thorium-impregnated tungsten matrix, which is heated by passage of current, serves as a source of thorium vapor. An opening in the shield can permits thorium vapor from this source to condense upon the filament and also upon the helices.

As is well known, deposition of thoruim on the tungsten filament causes its emission to rise by many orders of magnitude to a maximum value. If the filament temperature is not too high, and if the vacuum is good, this maximum emission will, of course, continue indefinitely.

If, however, the filament is raised for a period of time to some higher temperature, and then returned again to the original low temperature, it may be found that the high temperature has caused the evaporation of some of the thorium, and the electron emission will then be lower than it was before the high temperature treatment.

Fig. 2 shows data of this kind taken with the tube of Fig. 1.

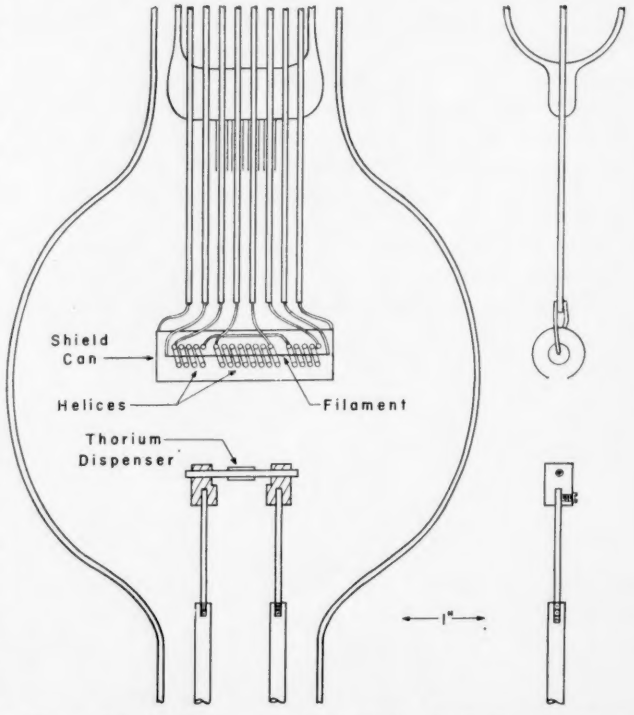

FIG. 1. Tube for studies concerning desorption of a thorium monolayer.

The temperature at which the electron emission was measured was 1045°C_B. At this temperature the maximum emission from the filament (whose area under the anode was $\frac{1}{8}$ cm²) was 2×10^{-4} A or 1.6 mA/cm². The horizontal line corresponds to that value of emission.

Having thus activated the filament by laying down an optimum thorium layer the experiment consisted in raising

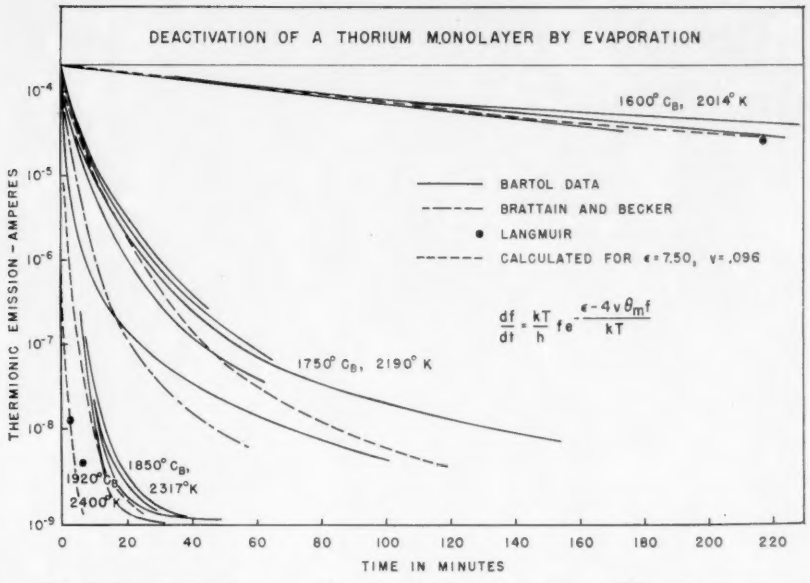

FIG. 2. Deactivation by evaporation of a thorium monolayer at different temperatures.

the filament to some higher temperatures for a given time, and then returning it to 1045°C_B and observing the emission. The uppermost curve in this figure shows the rate of deactivation which is caused by holding the filament at 1600°C_B, periodically returning it to 1045°C for measurements of emission.

Below this is a group of curves which show observed deactivation phenomena due to evaporation at 1750°C_B. The solid curves were all taken with the tube just described and one sees that the reproducibility is not all one might desire. The spread of data could not be ascribed to temperature uncertainties. We are inclined to attribute it to very minute traces of impurities still remaining in the tungsten after many days of electron bombardment ; impurities whose presence on the surface in varying degrees may be the cause of the differing values of evaporation rate.

Below the 1750°C_B data is a group of curves showing deactivation at 1850°C_B. Here too considerable lack of reproducibility is evident.

One sees that our data, given by solid curves, show an approximate sort of agreement with the observations made by Brattain and Becker[1] and by Langmuir[2] some thirty years ago.

Theoretical remarks

Time will not permit discussion of evaporation theory in this paper. It has been found, however, that within the existing uncertainties, the data conform to an expression obtained by integrating the equation shown in Fig. 2, where f is the relative coverage, ε the binding energy to the surface, v the repulsion energy between thorium atoms adsorbed on nearest neighbor sites, and θ_m is the fraction of total number of sites occupied when the thermionic emission is a maximum. This expression was derived from material in the book : " Theory of Rate Processes ", by Glasstone, Laidler, and Eyring.

The quantity f, we should perhaps explain, is proportional to the actual, absolute coverage, but up to this point in this paper, the constant of proportionality remains undetermined. By definition, f is equal to unity for that value of coverage, whatever it may be, for which the thermionic emission is at its maximum.

The dashed curves in Fig. 2 were obtained by integrating the equation shown, and then transforming the resulting coverage-vs.-time relation into an emission-vs.-time relation, using for this purpose the experimentally determined relationship between emission and the relative coverage f. A reasonable fit with existing data was obtained using a binding energy of 7.5 V and a value of the product $v\,\theta_m$ of about 0.1 V.

Evaporation data presented

Thus far, nothing has been said regarding the absolute significance of these deactivation curves in terms of the actual amount of thorium on the surface, or the actual evaporation rates in terms of grams leaving a square centimeter per unit of time.

During the past year we have carried through a direct experimental determination of that surface density of thorium which corresponds to maximum thermionic emission. Using this information and using the mathematical expression just referred to, we are now in a position to make some plots of actual evaporation rates in terms of temperature and absolute coverage and to relate evaporation data to electron emission.

In Fig. 3 are placed, side by side, charts of emission vs. coverage, for several values of temperature, and evaporation vs. coverage and temperature. These evaporation data are plotted from the mathematical expression which yielded the dashed curves of Fig. 2, and cover the range between 0.1 mg/cm² per century at 1250° up to 0.1 mg/cm² per hour at 2000°C_B.

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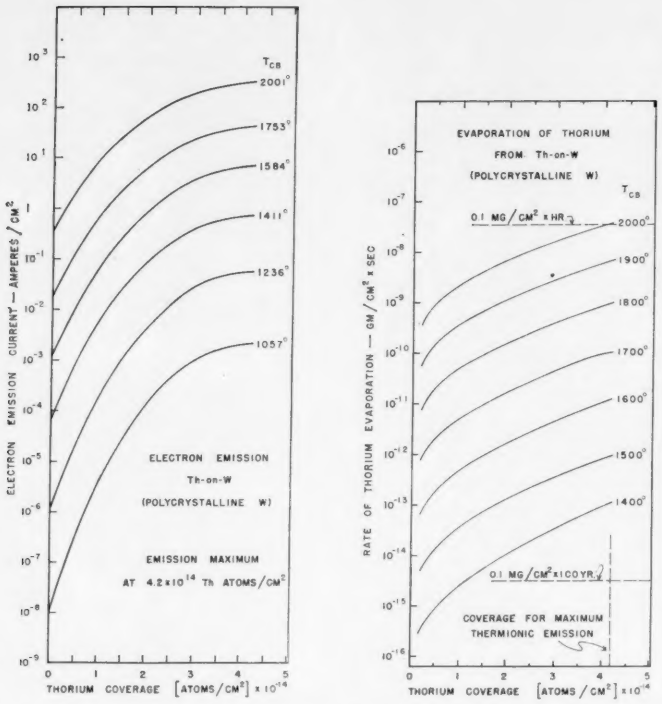

FIG. 3. Electron emission and thorium evaporation rate from a thorium monolayer on tungsten, as a function of absolute coverage for several values of temperature.

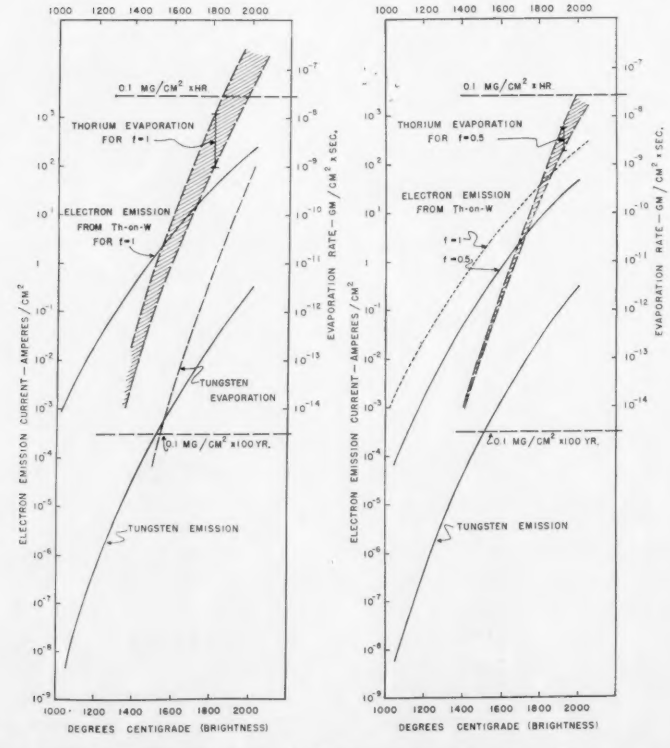

FIG. 4. Electron emission and thorium evaporation from a thorium monolayer, plotted for convenient comparison, as a function of temperature.

A more pictorial comparison of evaporation and emission is given in Fig. 4 and in these diagrams is also presented our estimate of the uncertainty in the evaporation data which exists at the present time. The upper boundary of the shaded area is the data of Ahearn and Becker[3] of 1938 which data seem to be the highest in the literature. The lower boundary is the data given by our own mathematical expression.

Figures 4a and 4b both show emission and evaporation from a thorium monolayer. Figure 4a shows these properties when the thorium coverage is that which corresponds to maximum thermionic emission ; in Fig. 4b the coverage is one-half of that amount.

Emission and evaporation from tungsten are included on the same diagrams.

Examination of this figure shows that, for a thorium monolayer with no other means of retarding evaporation, the evaporation becomes excessive for most applications when the 100 A/cm^2 emission level is approached. At 10 A/cm^2, evaporation will be somewhere between 0.6 and 6.0×10^{-10} g/cm^{2}sec or $(2-20) \times 10^{-4}$ mg/cm^2 hr. At 10 A/cm^2 the evaporation from 1 cm^2 would be in the neighborhood of 1 mg in a period of time somewhere between 500 and 5000 hr depending upon what surface conditions are present in the case being considered.

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Desorption by electron bombardment

We turn now to the subject of desorption by electron bombardment. This matter was previously reported upon in March of 1959 at the M.I.T. Conference on Physical Electrons at which time we had concluded that bombardment of the monolayer by electrons of 350 V energy or less did not remove adsorbed thorium atoms at a rate which we could detect. We calculated at that time that if any desorption of this kind existed it was too small to be of any importance in the matter of thorium dispenser cathodes. Since that report we have carried the experiment further, using the tube of Fig. 1, and I am now able to speak even more assuringly in this matter of electron desorption of the thorium layer. Using the tube shown, we were able to continue the bombardment for a total of 80 A hr/cm^2. And it is concluded that such desorption as might exist must have been less than 4×10^{-11} electrons removed per bombarding electron. This total bombardment of 80 A hr/cm^2 is of the order of magnitude of the total bombardment which might be experienced in reasonable life of a CW magnetron. And during this period the number of atoms/cm^2 removed, if any, was not more than 10^{13} or a very small fraction of one complete monolayer. It may therefore be concluded that removal of electrons by bombardment is of no practical importance even though the cathode concerned be a single and non-replenished layer of thorium atoms. In practical cases the loss of thorium by electron bombardment is probably considerably less than that lost either by thermal evaporation or by the residual ion bombardment from the imperfect vacuum.

It is evident that desorption of thorium by electron bombardment occurs at such a small rate that it need not be considered by the cathode engineer.

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Emission and Evaporation Properties of a Barium Calcium Aluminate Impregnated Cathode as a Function of its Composition

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Introduction

There are several factors which influence the emission and evaporation of impregnated cathodes. One of the major factors is the composition of the impregnant. The data presented here show the effects of varying the composition of BaO, CaO, Al_2O_3, and SiO_2 over rather wide limits. Some data on the effects of porosity are also shown. The evaporation rate was measured by an optical technique.

Cathode preparation

Porous tungsten cylinders were fabricated by pressing fine tungsten powder (4μ average particle size) at 12 tons/in^2 and sintering these at 2350°C in dry hydrogen. The porous tungsten slugs were impregnated with copper to make them machinable. After machining the copper was removed by acid leaching and vacuum firing. The resulting matrix had a porosity in the range of 20 to 25 per cent, calculated from the amount of copper removed and the densities of tungsten and copper at the melting point of copper. This assumes that the pores of the tungsten are completely filled with molten copper and that the copper is all removed. Independent metallurgical and chemical analyses indicate that these assumptions are valid. The aluminates were prepared by fusing mixtures of alkaline earth carbonates with alumina and silica. The i.d. of the porous tungsten cylinders were packed with the barium aluminate compounds, and they were impregnated in a dry hydrogen atmosphere at 1800°C or 100°C over the melting point of the aluminate, whichever was higher.

Construction of the emission and evaporation diodes

The diode was constructed as shown in Fig. 1. The cathode, 0.220 in. long × 0.120 in. o.d., × 0.090 in. i.d. was mounted 0.025 in. below a sheet molybdenum anode.

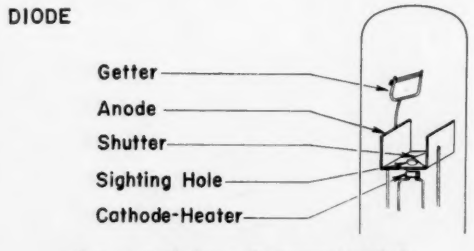

FIG. 1. Emission and evaporation diode.

A sighting hole is provided in the anode so that the cathode temperature can be measured with an optical pyrometer. A movable shutter covers this hole to keep the evaporation from clouding the area of glass through which the temperature measurements are made. An alumina coated heater is used.

Evaporation measurements

The cathode evaporation collects on the glass wall. If the apparent temperature of a constant temperature light source is measured through this film with an optical pyrometer, as shown in Fig. 2, the apparent temperature will be

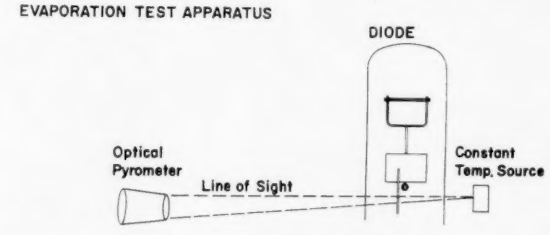

FIG. 2. Evaporation test apparatus.

reduced by an amount depending upon the type and amount of the evaporant. By applying Wien's law for the intensity of monochromatic radiation and Lambert's law for transmitted radiation, a correlation between apparent temperature and coating thickness can be obtained. Then a quantitative analysis of the amount of evaporant on the glass wall and a knowledge of the tube geometry will give a correlation between apparent temperature and amount of evaporation. Figure 3 shows this correlation for a nickel sleeve inside a

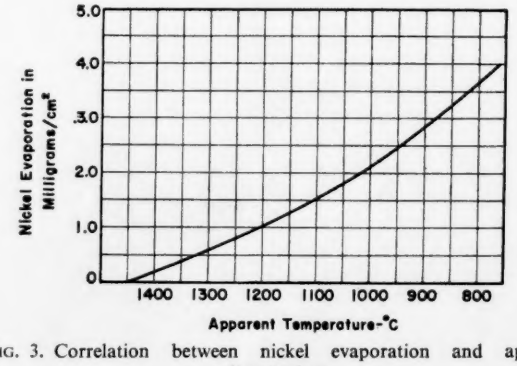

FIG. 3. Correlation between nickel evaporation and apparent temperature.

1.4 in. i.d. glass bulb. With a clean nonex envelope, the apparent temperature of a 1480°C$_{Br}$ source is 1452°C.

The method has certain advantages over the Knudsen cell method for measuring evaporation rates (and vapor pressures) of cathode materials. The total evaporation is measured periodically during life ; so the rate vs. time is easily calculated. There are no materials foreign to the cathode structure to obscure the results. These diodes are fairly simple to fabricate and test. The cathode emission is usually measured concurrently with the evaporation ; so information is obtained on emission, evaporation and life from the same tube.

In a Knudsen cell one measures the equilibrium vapor pressure of the cathode materials, and their reaction products with the cell material, averaged over a run. More equipment is needed, and several runs have to be made in order to get the same amount of evaporation information that can be obtained from one tube. A separate experiment is needed to obtain the emission and life data.

In comparison to the Becker[1] method for measuring evaporation rate, this one is simpler and it can be used for other than low work function materials ; but it does not give a precise figure for the instantaneous evaporation rate.

To verify the validity of this method, four tubes using nickel cylinders in place of cathodes were made. The evaporation rates of these at around 1000°C agreed well with the values reported in the literature[2], the average deviation corresponding to a difference in operating temperatures of 9°C.

The major source of error appears to be in obtaining the correct correlation between the temperature reading and the amount of evaporation for the proper type of evaporant. A precise and accurate chemical analysis for a few micrograms of barium is needed. Also the light absorbing power of Ba is much higher than that of BaO ; so if the ratio of Ba to BaO is changed the calibration is no longer valid. The latter problem does not occur with passive materials such as nickel.

Test conditions

The tubes were constructed and exhausted according to the procedures outlined in papers Nr. 25 and 28. The cathodes were outgassed at 1150°C for ½ hr, the anodes were heated with r.f., the tubes were sealed off, and the barium type getters were flashed. On the aging rack the cathode is operated at 1100°C$_{Br}$ and space charge limited emission is drawn. The cathode is periodically cooled to 925°C where nearly temperature limited emission can be drawn momentarily without overheating the anode. Non-symmetrical geometry makes emission density measurements

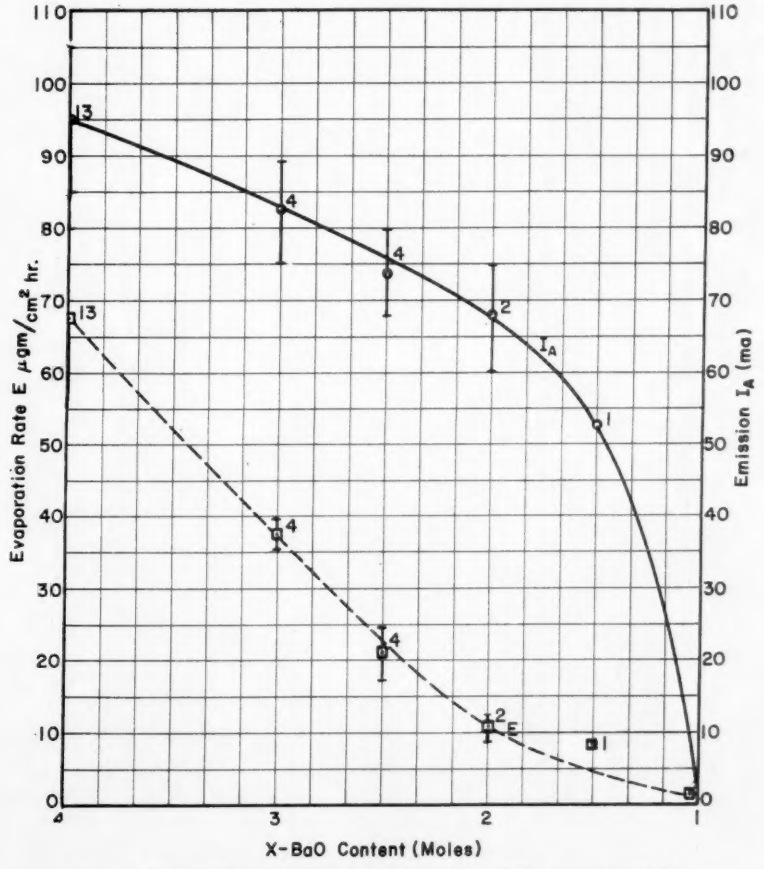

FIG. 4. Evaporation rate (E) and emission (I_A) vs. BaO content (moles) in XBaO.1CaO.1Al_2O_3.

difficult, but the relative values are a good indication of the saturated emission. The evaporation measurements were also made periodically during life. The average evaporation rate over the first 50 hr of life is reported here. Throughout this paper a 3–1–1 ratio means a ratio of 3 moles of BaO, to 1 mole of CaO, to 1 mole of Al_2O_3 in that order.

Results

Figure 4 shows how the emission and evaporation varied when the BaO content was varied from 1 to 4 moles while holding the CaO and Al_2O_3 content constant at 1 mole each. In these curves, the length of the vertical line through each point indicates the average deviation and the number beside the point indicates the number of samples. The curves show that as the BaO content was reduced from 4 to 2 moles, the evaporation rate fell by a factor of 6 to 1. At the same time, the emission only decreased about 30 per cent. At a ratio of 1.5–1–1 the emission was decreased significantly and at 1–1–1 the emission was very low. It appears that about 1.5 to 2 moles of BaO are required to obtain good emission. By checking the emission at the low temperature of 925°C, any slight variation in activation is very noticeable.

The data from Brodie and Jenkins[3] in *J. Electronics*, March, 1957, and using their later calibration[4] show a barium evaporation rate of 13μg/cm^2 hr for a 3–1–1 cathode at 1145°C as compared to 37μ g/cm^2 hr for our data. The true temperature was obtained by using an experimentally determined figure of 0.66 for the spectral emissivity of the cathode and a 7°C correction for the absorption of the glass wall.

Figure 5 illustrates the changes in emission and evaporation due to the addition of various amounts of CaO to 4–0–1 aluminate. There is both a large decrease in evaporation and a large increase in emission as the CaO content is increased from 0 to 1 mole, but there is little change when the CaO content is increased above one mole. Other tests have shown that CaO makes the cathode more hydroscopic. This presents problems such as cracking of the cathode when exposed to moisture, etc. These results agree with those found in the literature[3–6]. It is postulated[5] that the very refractory CaO increases the emission from the ends of the pores, but we have not observed any significant increase in either d.c. or pulsed emission as the porosity is varied from less than 20 to over 50 per cent. Without the CaO the evaporation rate is very high. Brodie and Jenkins[3] show a rate of 210μg/cm^2 hr for 3.7–0–1, which is similar to 290μ g/cm^2 hr for 4–0–1 shown here. The large decrease in evaporation caused by the CaO is difficult to explain.

X-ray diffraction data obtained in this laboratory show that the crystal structure of $3(BaO.CaO).1Al_2O_3$ does not change as the CaO content is varied from 0 to 0.3 moles.

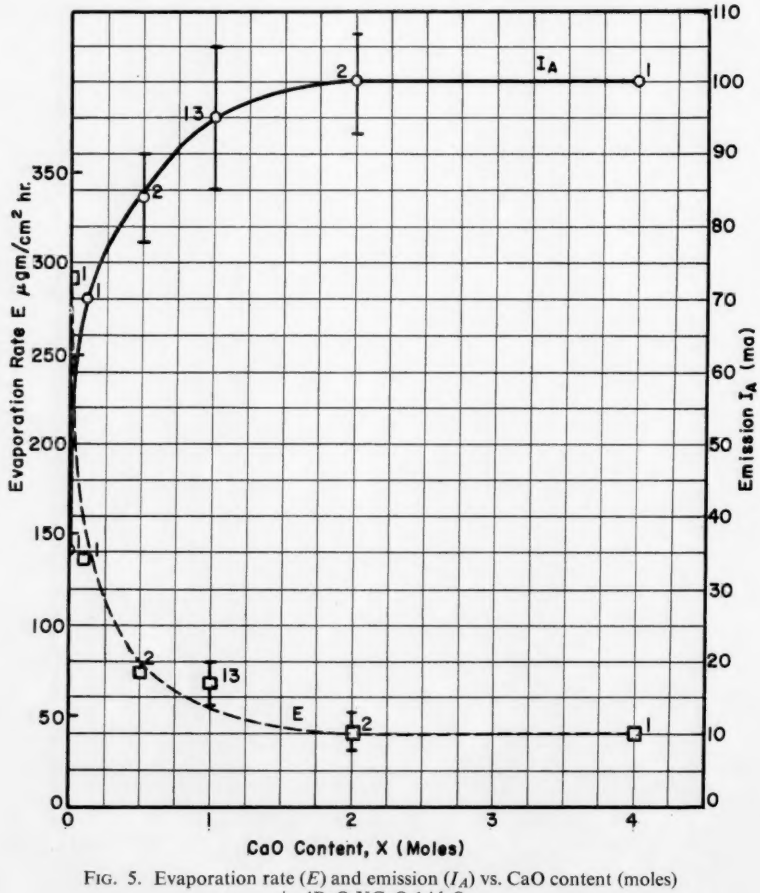

FIG. 5. Evaporation rate (E) and emission (I_A) vs. CaO content (moles) in $4BaO.XCaO.1Al_2O_3$.

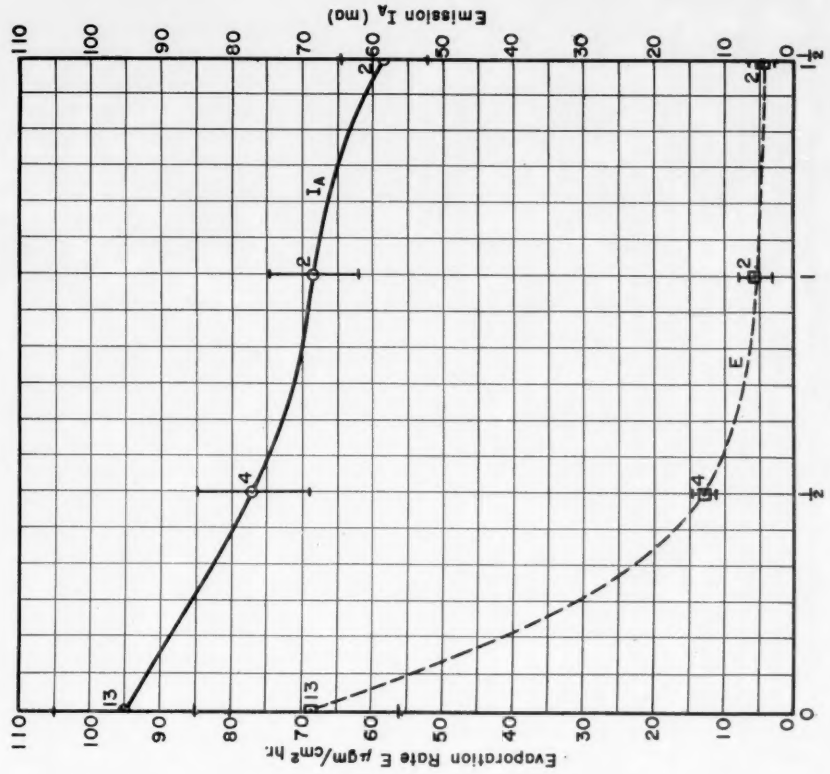

FIG. 7. Evaporation rate (E) and emission (I_A) vs. SiO_2 content (moles) in $4BaO.1CaO.1Al_2O_3.XSiO_2$.

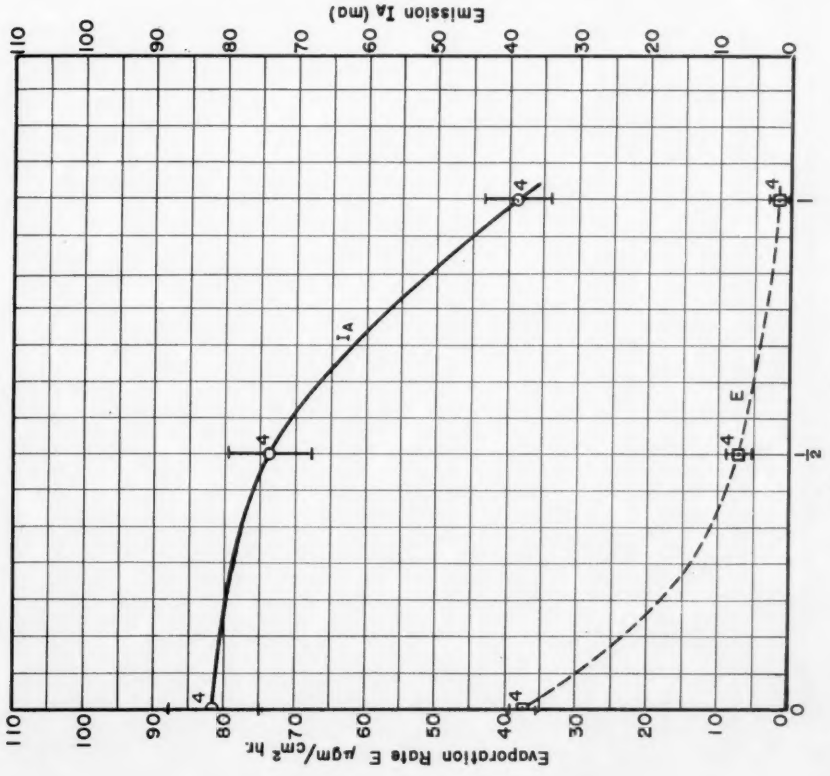

FIG. 6. Evaporation rate (E) and emission (I_A) vs. SiO_2 content (moles) in $3BaO.1CaO.1Al_2O_3.XSiO_2$.

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At about 0.4 moles of CaO there is a definite shift in the diffraction patterns. This seems to offer no clue to the role played by the CaO, because even 0.1 moles of CaO has a definite effect upon emission and evaporation.

The effects of adding SiO_2 to a 3–1–1 mixture are shown in Fig. 6. The addition of $\frac{1}{2}$ mole of SiO_2 results in about one-fifth the evaporation of the 3–1–1 mixture. The addition of one mole of SiO_2 reduces evaporation still more, but emission appears to be seriously impaired. The emission of the 3–1–1 mixture with $\frac{1}{2}$ mole SiO_2 is only about 10 per cent less than the 3–1–1 mixture itself.

Figure 7 shows the effects of adding various amounts of SiO_2 to a 4–1–1 mixture. Again the addition of $\frac{1}{2}$ mole of SiO_2 reduces the evaporation approximately fivefold, but only decreases the emission by about 20 per cent. One mole cuts the evaporation in half again and only reduces the emission by another 10 per cent. Amounts in excess of one mole have little effect upon evaporation, but decrease the emission still more.

Although some of the emission reductions may seem large, the cathode can produce current densities of more than 10 A/cm^2. Consequently, a small reduction in emission may be tolerated by many applications to gain the large reduction in evaporation.

Effects of porosity upon evaporation rate

Figure 8 shows the average evaporation rate vs. porosity for a 4–1–1 cathode operating at 1050°C$_{Br}$. This was the average rate for the first 100 hr of life. The curve represents the average of forty samples with porosities ranging from 12 to 28 per cent. The general increase in evaporation with increasing porosity has also been noticed for other compositions of the impregnant and for much higher porosities.

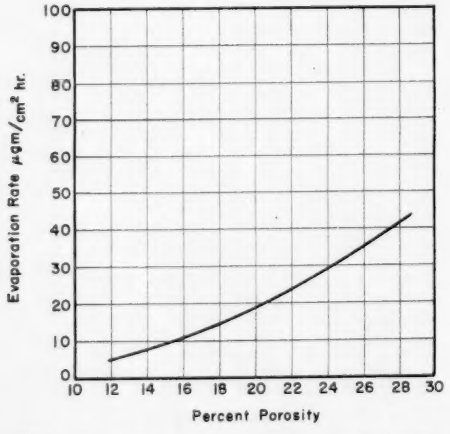

FIG. 8. Effect of porosity upon evaporation rate of a 4BaO.1CaO.1Al_2O_3 impregnated cathode at 1050°C$_{Br}$. Average evaporation rate during first 100 hr of life.

The porosity was varied by varying the particle size of the tungsten powder and the forming pressure. The d.c. emission and life of these cathodes did not appear to be a function of the porosity. Cathodes having less than 15 per cent porosity were difficult to impregnate reproducibly, and some had low emission. The data from the poorly impregnated cathodes were not used in plotting the curve.

Brodie *et al.*[4] observed a 3 to 1 decrease in evaporation rate as the porosity was increased from 25 to 45 per cent, while we observed a large increase in evaporation with increasing porosity. Their average pore size was less than 1μ for the 25 per cent porosity cathodes and several microns for the 45 per cent porosity cathodes. Our average pore size was 3 to 4μ for the 20–25 per cent porosity cathodes, and it also increased with increasing porosity. Our data was taken with a 4–1–1 aluminate while theirs was taken with a 3–$\frac{1}{2}$–1 aluminate.

Conclusions

The evaporation rates reported here for the barium aluminate without calcium oxide are similar to those reported by Brodie *et al.*[3, 4] The addition of CaO of 0.5–1.0 moles is desirable from both the emission and evaporation standpoint. The BaO content should be in the order of 2.0 moles or over. The addition of SiO_2 up to about 0.5 moles is desirable from the evaporation standpoint, but it does have a slight harmful effect upon emission.

Acknowledgments

I wish to acknowledge the assistance of Mr. D. Pitman for performing the X-ray diffraction studies and Messrs. A. Amato, A. Newfell and L. Lanzarotto for assistance in the experimental aspects of the work.

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Omegatron Investigation of the Gas Ambient in Laboratory Diodes having Oxide Coated Cathodes

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1. Introduction

The course of certain electrical defects in vacuum tubes has often been related to the nature of the gas ambient in the tube. Much valuable information concerning effects of various gases on oxide cathodes has already been deduced from techniques involving the introduction of known amounts of specific gases into either oxide[1-4] cathode or matrix[5] cathode systems. Through the creation of conditions designed to alter emission levels such experiments serve the useful function of advancing our understanding of the mechanism of thermionic emission. However, another aspect of the overall problem is what is now generally recognized as being the dynamic or transient nature of gases normally encountered in vacuum tube devices. Conventional mass spectrometers have been applied to this problem by Plumlee and Smith[6]. On the other hand, mass spectrometers such as omegatrons are small enough to be employed as part of the same vacuum tube envelope and are readily adaptable and reliable for the analysis of gases during simultaneous life studies of a number of vacuum devices. This paper reports the results of such work. A further property that makes the omegatron well suited for this type of work is its simplicity of construction which permits thorough outgassing and its low unit cost.

The results of our omegatron-diode investigations provide evidence for the existence of adsorption and desorption phenomena for most of the commonly found gases and also reveal a number of chemical equilibria involving, in particular, hydrogen and/or carbon-containing gases. The multiplicity of types of surfaces, even in our relatively simple laboratory diode, and the presence of hot tungsten filamentary heater structures, all provide a basis for dynamic gas processes throughout the life of the device. The relationship of the thermionic emission to changes in the gas ambient was examined against this background. Recognizing that cathode reactions themselves are sufficiently complex, it was decided that a simple diode should be employed and that the initial study be restricted to an examination of the response of oxide cathodes to what was observed to be a continuously changing gas environment during several thousands of hours of laboratory diode operation. The data are preliminary in the sense that these experiments were designed to answer a limited number of initial but basic questions with regard to the behavior of gases in tubes. Those answers that were successfully sought will be described. Evidence of a methane–hydrogen relation will be established. The role of small concentrations of carbon monoxide that were found will also be described.

One of the major objectives was to determine the extent to which the oxide cathode responds to and reacts with those gases in its natural environment, and for this reason conventional flash type getters were not used in most of the diode-omegatron twin tubes. Some data from a limited number of gettered tubes also will be shown for comparison, but the main study was restricted to the less complicated getter-free system. The diagnostic tools used include omegatron mass spectrometry, pulsed emission and shot noise techniques.

2. Pulsed emission, shot noise and omegatron measurements

The cathode and gas studies were made with the diodes* and omegatrons† sealed in a common envelop‡ (Fig. 1). Electron emission was measured at a cathode temperature of 1000 °K using 1000 V square wave 10-μsec pulses at two per second. Additional information on emission uniformity was provided by monitoring the 30-Mc shot noise component of a 5-mA plate current while scanning the cathode temperature from 1000 °K down to 750 °K and thereby examining the transition region between space charge and saturation operation.§ The need for such additional data is based upon past observations which indicate that pulsed emission alone does not adequately represent the electronic properties of oxide cathodes unless there is also independent evidence of

*The diode features an independent anode heater, a knife-edge tube closure and a Pt/Pt-10 per cent Rh thermocouple welded to the inside roof of the cathode cap. These features facilitated effective application of various processing controls. An active nickel, designated as N-4, coated with Sylvania C-10 triple carbonate was used. The anode–cathode spacing (0.020 in.) is maintained by locating two quartz cylinders between an Al_2O_3 disc and the pure nickel anode disc. The cathode is secured to the disc by tungsten straps.

†The omegatron was constructed of molybdenum electrodes with a tungsten filament. The normal operating conditions were : magnet field 6000 gauss, r.f. volatge 1.7, trapping voltage 1.0, electron beam 1.0 μA, electron collector bias 22 V, and electron accelerating voltage 70 V.

‡The separation of the spectrometer from the diode section as shown in Fig. 1 is in contrast to Plumlee's arrangement[6] (Fig. 1) where the cathode is in close proximity to the ion beam of the spectrometer. This may account for the difference in detectability of such adsorbable gases as Cl_2 and O_2. On the other, the finding with respect to CO is comparable in both cases.

§Further details of this measurement appear in Paper 22 presented at the conference.

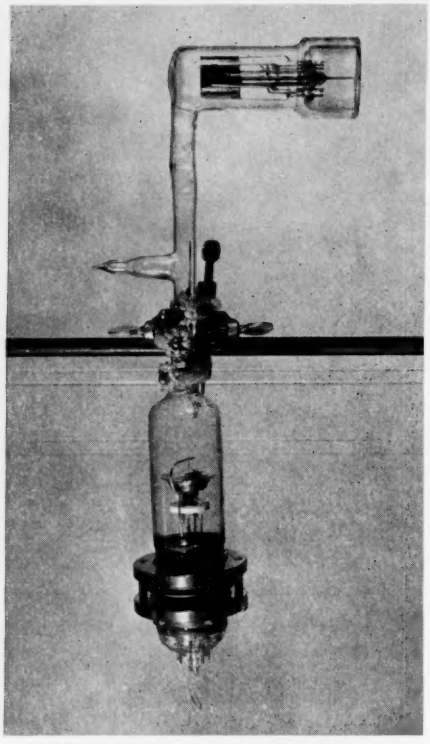

FIG. 1. Diode-omegatron twin tube.

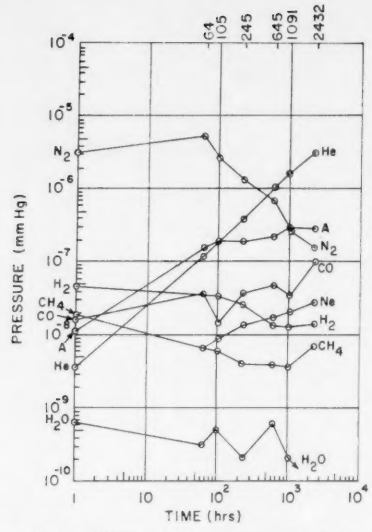

FIG. 2a. Gas ambient as a function of life (getter absent).

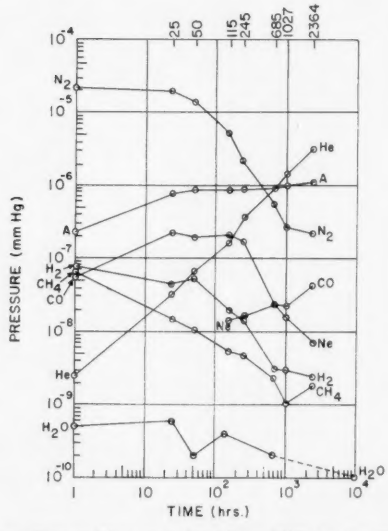

FIG. 3a. Gas ambient as a function of life (getter absent).

the relative uniformity of the work function. Both shot noise and pulsed emission were therefore measured at frequent test periods* during life. The test sequence each time was the emission test, omegatron scan with the cathode at 1000°K and finally again an emission test to uncover possible evidence of instability. When slight changes occurred in some instances they were subsequently traced to improper handling of the shot noise test and no direct effect could be attributed to the operation of the omegatron in the presence of the oxide cathode. The recorded peak heights of specific masses during the omegatron scan thus provided a quantitative as well as a qualitative knowledge of the gases at a particular time. The pressure data in the figures are actually $10^5 \times$ the ion current in amperes per microampere of electron beam current, assignable to the principal ion of each gas. The factor 10^5 is nearly correct for converting the ion current to mmHg for nitrogen and approximately correct for other gases. The use of this factor for all gases retains a simple relation to the primary data, gives values in accord with ion gauge reading, and allows the use of the familiar pressure scale, rather than an ion-current scale, in presenting the data.

3. The gas ambient in ungettered diodes

The life test records of the diode samples shown in Figs. 2a and 3a are typical of gas patterns observed in diodes over a similar period of thousands of hours. Oxygen and carbon dioxide were absent consistently with respect to a detectable level of 10^{-10} mm in all analyses. The high rate of chemisorption of oxygen by hot tungsten present in both the diode and the ionization sections of the tube precludes any detection of oxygen. The initial appearance of high concentrations of nitrogen (10^{-6}–10^{-5} mm) may be a consequence of having stored all diodes and omegatrons in a dry nitrogen atmosphere prior to tube processing. Recent literature[7] on omegatron studies also reports an appreciable evolution of nitrogen. The marked decrease in nitrogen during life suggests either that it is cleaned up by the tungsten or that it forms a stable nitride[8] of barium at the cathode. Carbon monoxide was measured in most cases at pressures of 10^{-8}–10^{-7} mm throughout life. The CO pressure differences from tube to tube were found to be related to the emission properties of the cathode. An order of magnitude higher concentration of CO was detected in a single case illustrated in Fig. 3a, its effect on emission will be discussed in the following section.

*The test periods after zero hours were 50, 100, 250, 500, 1000, 2500 and in some cases 5000 hr. While on life, the cathode temperature was 1000°K and the plate voltage 15 V a.c. Deviations from this general schedule are indicated by the data appearing in the figures.

Hydrogen and methane pressures are generally very similar both initially and in terms of the rate at which they decrease during life from about 10^{-8} mm or slightly higher down to about 10^{-9} mm. Water vapor pressures are below 10^{-9} mm during life and because the peaks are near the noise level of the instrument, the apparent ranges do not appear to be significant.

Inert gases such as argon, helium and neon were found to have generally consistent concentration patterns during life. The increase in helium is in accordance with known leak rates through glass. Neon tends to increase to pressures of about 10^{-9} mm after approximately 100 hr of tube operation. Argon was more erratic in occurrence until it was found that the quartz spacers constituted a virtual but variable argon leak. Subsequent notching of the quartz significantly lowered initial argon pressures and resulted in more consistent behavior during life from tube to tube and in individual tubes. Preparatory to these analyses, the entire glass envelop and tubulation of each tube was maintained at a temperature of 150°C throughout processing in an attempt to minimize any subsequent desorption from the walls.

4. The relationship between the gas ambient and emission in ungettered tubes

Thermionic emission was evaluated by two techniques, pulsed and shot noise. A discussion of the relative merits of pulsed emission measurements is not relevent to the main subject of this paper, but it should be indicated that recent experience has shown that pulsed emission data are very often inadequate to define the electronic properties of the oxide cathode system, and that an examination of the shot noise component of the current in the transition region between space charge and saturation offers significant supplementary data. For this reason, shot noise–temperature scan curves and pulsed emission data obtained at regular intervals during life have been combined as shown in Figs. 2b and 3b. Pulsed emission values in A/cm² at 1000 V and at 1000°K appear parenthetically at the ends of the appropriate curves. Generally, any improvement in emission during life will shift the noise curves toward the left, while a deterioration in emission will move the curves to the right irrespective of the pulsed emission level. In most cases pulsed emission data are consistent with the interpretation based upon shot noise characteristics, but some striking exceptions are observed when inhomogeneities in work functions are involved.

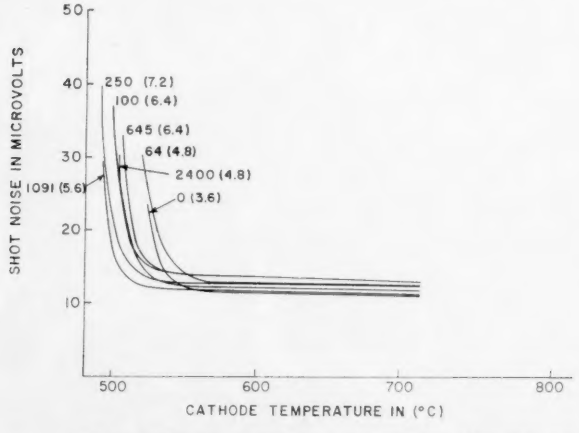

FIG. 2b. Shot noise vs. cathode temp. during life.

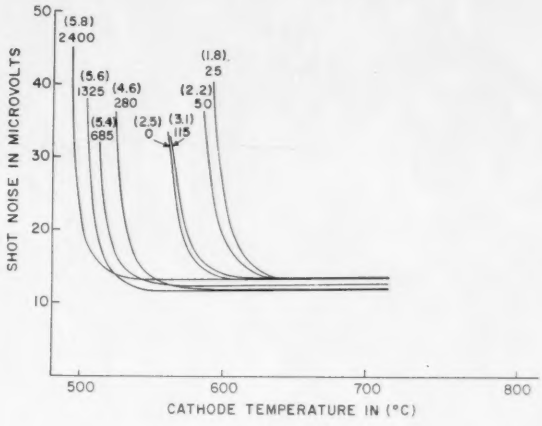

FIG. 3b. Shot noise vs. cathode temp. during life.

While it may appear that emission generally tends to increase during the life of these diodes, and that during this time the nitrogen pressure decreases, no direct connection has been proved from our data. A closer examination of the data does indicate that changes in emission have been influenced by changes in carbon monoxide pressure. Fig. 2b illustrates a progressive improvement in emission up to and including the 1000 hr period, but also indicates that some deactivation has occurred by the next test period, 2500 hr. Pulsed emission data do not reflect such changes with absolute fidelity, but the correlation is evident. During this same period the CO pressure (Fig. 2a) increased abruptly to a pressure approaching 10^{-7} mm. This pressure appears to be a critical one in terms of thermionic emission ; it is further illustrated in Figs. 3a and 3b, in which the emission is substantially depressed during the early periods of life. The CO pressures are again in the 10^{-7} mm region until 100 hr have elapsed. While the CO pressure remains in this range at 250 hr, cathode recovery has already appeared to be under way with further improvement clearly indicated as the CO pressure decreases further. These pressure measurements, like all those that have been described, were obtained while the cathode was operated without current drain in this case and at 1000°K, the same temperature as used during life test. Later measurements in which the effects of cathode temperature on the gas ambient were studied, indicate that the CO decreases only slightly when the cathode cools to room temperature and that the pressure returns to about the original higher level upon reheating the cathode. Raising the cathode temperature to 1100°K in the presence of these pressures of CO resulted in a further temporary reduction in emission which is consistent with the view[9] that the

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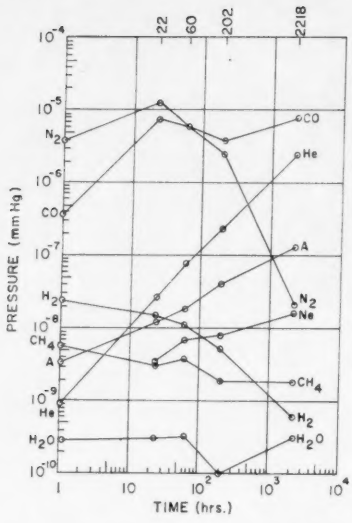

FIG. 4a. Gas ambient as a function of life (getter absent).

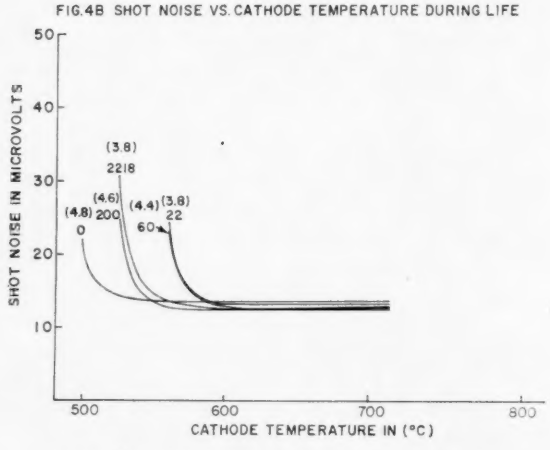
FIG.4B SHOT NOISE VS. CATHODE TEMPERATURE DURING LIFE
SHOT NOISE IN MICROVOLTS
CATHODE TEMPERATURE IN (°C)
(3.8) 2218
(4.6) 200
(4.4) 60
(3.8) 22
(4.8) 0
PULSED EMISSION IN AMPS/CM² AT 1000°K IS INDICATED PARENTHETICALLY. THE TIME AT WHICH EACH CURVE WAS OBTAINED IS ALSO SHOWN.

FIG. 4b. Shot noise vs. cathode temp. during life.

poisoning rate by CO at a given pressure is increased with increasing temperature. Figs. 4a and 4b illustrate a more extreme example involving the effect of a higher CO pressure on thermionic emission. In this case, the pressure increases well into 10^{-6} mm region, and recovery to the original state of activation is never achieved completely during subsequent life. Again pulsed emission does not appear to be a particularly sensitive indicator in this instance, although the shot noise curves reveal significant changes during the attempted but unsuccessful recovery period. The shot noise curves also appear to indicate a decrease in the uniformity of the work function.

The source of the CO and the manner of its pressure decrease have not been sought in these experiments. With reaction temperatures held constant at the cathode, the variation in initial CO concentration in the gas phase from tube to tube could be due to a source other than the cathode. The anode is more suspect in this case, because anode temperatures were monitored optically and were therefore not under precise control during processing. Possible variations in amounts of CO originally adsorbed on and subsequently desorbed from the anode could contribute to such effects. The mechanisms of poisoning by CO have been discussed in the literature in terms of temperature and core material dependence, and our experiments did not attempt to offer further grounds for speculation. The tendency toward recovery from CO poisoning as the CO pressures decrease appears to be persistent and is presumably the result of employing an active type of cathode nickel (N-4) for these experiments.

5. Gas ambient and emission in gettered diodes

Barium getters effectively reduced the concentration of all except the rare gases in the diode-omegatron envelop early in life. Two examples are illustrated in Fig. 5a and Fig. 6a. In most cases, the pressures are below 10^{-8} mm and are in the 10^{-9} mm region at 1000 hr of operation. The emission levels do not necessarily reflect the small differences in residual gas pressures in these tubes. Figs. 5b and 6b show

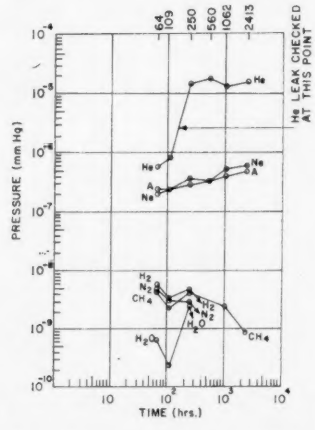

FIG. 5a. Gas ambient as a function of life (gettered).

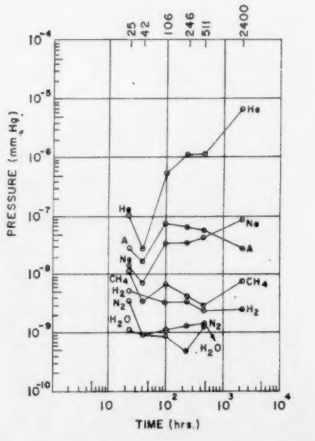

FIG. 6a. Gas ambient as a function of life (gettered).

changes in the pulsed emission during life ; corresponding shot noise data are only available at the 1000 hr period.

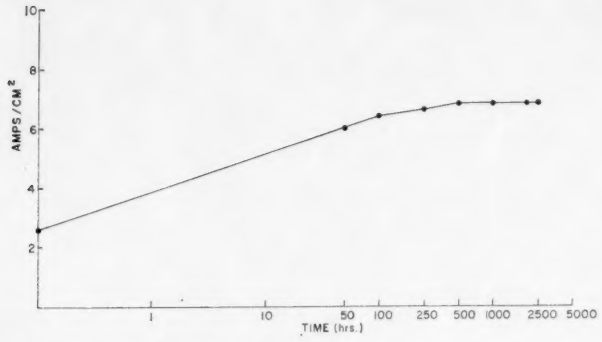

FIG. 5b. Pulsed emission density at 1000°K during life.

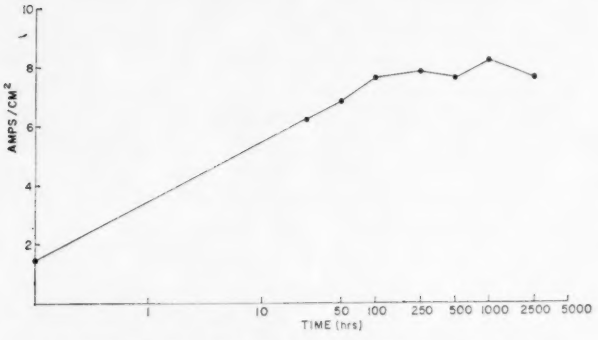

FIG. 6b. Pulsed emission density at 1000°K during life.

6. The gas ambient as a function of cathode temperature

When residual gases were analyzed periodically in ungettered tubes as a function of several cathode temperatures it was found that the most significant effects were those involving nitrogen, carbon monoxide, hydrogen and methane. The inert gas pressures did not change with cathode temperature. With the exception of methane, the pressures of the remaining gases increase with increasing cathode temperature and decrease with decreasing temperature. Methane pressures tend to decrease with increasing cathode temperature after desorption has taken place. Conversely, cooling the cathode produces an increase in methane and a decrease in hydrogen pressures. Independent studies of the response of tungsten filaments to temperature changes in comparable high-temperature regions indicate a similar inverse relationship between hydrogen and methane, which may be by way of chemical reactions involving the carbon in the tungsten. The chemical reaction :

$$C + 2H_2 \underset{\text{high temp.}}{\overset{\text{low temp.}}{\rightleftharpoons}} CH_4$$

is suggested as the controlling process.

The final pressures of hydrogen and methane both tend to be higher after cooling than they were before heating and this requires an additional supply of both carbon and hydrogen.

With long continued heating and repeated cycling, methane and hydrogen tend to disappear. As carbon is presumably still available at the heater, it is the removal of hydrogen that must be accounted for. In any case, even after methane and hydrogen do not appear on cycling from 300°K to 1000°K to 300°K they may reappear on cycling to 1100°K possibly because of the additional release of hydrogen.

The irregularity in the measured amounts of methane and its pressure change on heating might be explained as follows : methane is adsorbed at surfaces, preferably cooler surfaces. When the tube is removed from life test and the cathode cools methane moves from other surfaces, in part, to the cleaner cathode and heater surfaces. On heating this methane may be driven off rather than decomposed to any extent. This effect is greater the longer the tube has been left cold. When this is the predominant effect heating the cathode gives an initial rise in methane pressure which may be quite large.

To avoid this effect in recent work an effort has been made to transfer tubes quickly from the life rack to the omegatron test stand and to immediately reheat the cathode without taking time for scanning the spectrum with the cathode cold. This gives the closest estimate of actual life test conditions.

Nitrogen pressure also undergoes changes in cycling the cathode temperature. On initially heating the cathode it either tends to rise, if present, or appear if it was absent. On cooling, it tends to fall or even disappear. Long heating or repeated cycling tends to reduce the nitrogen pressure but cycling to a still higher temperature may make it reappear. Surface adsorption, without the migration effects seen for methane, can account for much of the nitrogen behavior.

Acknowledgment

The authors gratefully acknowledge the proficiency of the technical staff which includes Miss A. Woods, Messrs. E. Boyd, E. Cote and J. M. Lech in their respective tasks of tube fabrication and processing, emission and noise measurements and mass spectrometric measurements.

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Vacuum Techniques in Europe

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1. Introduction

Nowadays vacuum technique covers an extremely large field and people of widely different interests are studying this sometimes very exciting subject. I only need to remind you of the First International Congress on Vacuum Techniques, held two years ago at Namur. The Proceedings of this congress, consisting of two big volumes with more than 800 pages in all and dealing with subjects ranging from ultra-high vacuum to vacuum concrete, as also of course with the problems of gas analysis and getters, may serve as an illustration.

Having been asked to speak about " Vacuum Techniques in Europe " I am subjected already to limitations of a geographical nature. But even then the field is too large. Moreover I am convinced that most of you will have only a limited interest in vacuum concrete or vacuum drying for example, which again will mean a welcome restriction. Reflecting on the question as to which subjects would be of most importance here I was confronted with the problem that although I had information about new, so far unpublished work in my own company, I could only speak about published work by other people, which would mean of course about their earlier work. To accomplish my task, I could have chosen a number of subjects which would have been of interest to you, e.g. ultra-high vacuum, leak detection, getter-ion pumps, gas analysis, getters, etc., and discussed the papers which have recently been published about these subjects. This would indeed have been a good approach, but I think more suited to a general and rather extensive survey and less suited to an occasion like this. What I want to do today is to give an impression of what in my opinion are the most important views prevailing in Europe, and the most important results that European laboratories have obtained over the past few years, and generally illustrate them by quoting from published papers. Of course this choice will be somewhat personal and somebody else in my place would have given a different talk ; he would have stressed or neglected other things, but I believe that the general picture of the situation would have been about the same.

To people making electron tubes, vacuum physics and chemistry are usually only of interest in so far as they help one to achieve and maintain good cathode activation. The main focus of interest is the interaction of the gas with structural features, and in particular with the cathode, but this interaction may also influence the surface condition of other electrodes. Besides this interaction there may also be interaction between gas molecules and electrons which may result in the formation of ions and so give rise to ion currents and in some cases to an increase in tube noise.

It is unquestionable that, as more and more is demanded of our cathodes, the need for better pumping methods becomes more urgent. Although theoretically one could argue that not all gases will be harmful to a cathode, so that only the partial pressure of a limited number of gases has to be kept below a certain limit, in practice this usually means that a very thorough treatment of components and a good pumping schedule must be applied. As an example I would like to mention some results which Mr. v. Iperen and I have obtained on a special type of dispenser cathode, an L-cathode with reduced rate of barium evaporation, which we want to use in a 2.5 mm reflex klystron. The cathode loading amounted to a current density of 8.5 A/cm^2 continuously. It was impossible to get satisfactory results when the test tubes were pumped to a level of 10^{-7}–10^{-6} Torr. With a better degassing and pumping procedure the pressure in the tube was reduced to values around 10^{-9} Torr and the behaviour of the cathodes under the given load was now completely satisfactory. Cathodes showing a greater barium supply and a higher rate of evaporation were hardly sensitive to these pressure differences.

As an example of the necessity of producing a low pressure in a tube to reduce noise I would like to mention the recent work of Smith with a backward-wave oscillator. He showed that a pressure above about 10^{-9} Torr in his tube resulted in a higher noise level due to ion oscillations in the existing electric and magnetic fields.

It goes without saying that knowledge of the total pressure alone is in most cases insufficient to provide better understanding of the phenomena encountered in a gas mixture. It is the gas composition, and hence the partial pressures of all the gases, which must be known if correct conclusions are to be drawn from the experiments. This holds not only in those cases where the gas atmosphere is found to effect the quality of the cathode but also for example in pump speed measurements at low pressures near the ultimate pressure of a pump. Gas analysis is in this case absolutely indispensable.

The items which I would like to discuss in particular are :

(1) pumps including ultra-high vacuum pumps

(2) gas analysis.

A number of papers on the various subjects to be discussed may be found in *Advances in Vacuum Science and Technology*, which are the Proceedings of the First International Congress

on Vacuum Technique held at Namur in 1958, and in *Vacuum, 10*, Nr. 1–2, which contains the Proceedings of the International Symposium on Residual Gases in Electron Tubes and Related High Vacuum Systems held at Como in 1959.

2. Pumps

(a) *Diffusion pumps*

It is now generally realized that curves of pumping speed against pressure or of throughput against pressure, as found in our pump suppliers catalogues have only a limited value. The speed values displayed, which are usually derived from the throughput and the pressure in the vicinity of the pump mouth, are influenced by the way in which this pressure is measured. So far no agreement has been reached internationally about the manner in which the pressure measurement must be made.

In Europe studies on this subject have been published by Oatley[1], Barre, Mongodin and Prévot[2], Degras[3] and myself[4] and here too there is no agreement. In my opinion part of the differences are of non-fundamental nature, as for example the question of the size of the test dome attached to the pump. About the real fundamentals, including the meaning of the term " pressure in the vicinity of the mouth " and whether it is really permissible to add the resistances constituting the gas path, more discussions will be needed before agreement can finally be reached.

The pumping speed becomes zero at the ultimate pressure. It was shown, however, more than ten years ago by Berry[5] that a pump works quite satisfactorily below the ultimate pressure for a gas, which is absent from or present only as a trace in the residual atmosphere. In fact at these low pressures all molecules in the gas phase behave individually and they are removed quite independently by the diffusion pump. When a certain ultimate pressure is found, an equilibrium exists for every sort of gas between the amount given off or produced and the amount removed by the pump. The gas source does not necessarily need to be the test chamber, it may also be the pump itself as is the case for the molecules of the operating fluid or of their decomposition products. The source may also be an ionization gauge which may, as you know, also act as a pump. On the influence of an ionization gauge with its hot filament on the gas composition I will speak later, but I hope I have already made it clear that one must be very cautious when judging pump speeds in the vicinity of the ultimate pressure.

The considerations just given led us a number of years ago to construct an all-glass bakeable system, the diffusion pump included[6]. As operating fluid we chose the old favourite mercury, as experiments had shown us that all oils then available decomposed when boiling into products, which could not be removed effectively by liquid nitrogen. A second diffusion pump was used as a backing pump to prevent back diffusion and very effective liquid nitrogen traps were constructed to prevent the mercury from entering the test chamber. These traps had a considerable conductance which allowed us to get a pump speed of about 10 l./sec at the entrance of the test chamber. We succeeded in getting what we wanted, very low pressures were achieved and we reached the X-ray limit of our gauge which was equivalent to a N_2 equivalent pressure of some 10^{-11} Torr. From a possible deviation from this limit we estimated the pressure to be below 10^{-12} Torr, N_2 equivalent, but in fact we had reached the limit of our ability to measure pressure. Although I do not believe that essentially new things were done in this experiment, it showed that classical methods could be used to investigate the ultra-high vacuum region and that the ultimate pressure of a diffusion pump could be shifted to very low values. We have used this system and we are still using it for investigations in the ultra-high vacuum region, and also for the evacuation of electron tubes. It is often argued that the liquid nitrogen is a nuisance. It depends of course on the application, but we do not consider the problem of the liquid nitrogen traps to be a very serious one.

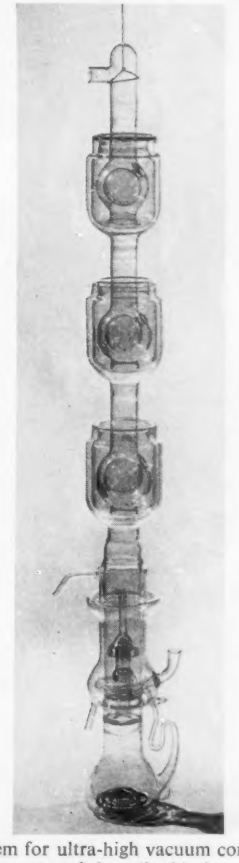

FIG. 1. All-glass system for ultra-high vacuum consisting of a mercury diffusion pump and three liquid nitrogen traps.

In the oil diffusion pump the problem of getting low pressures is, I believe, hardly more complicated, although one has to employ different methods owing to the decomposition of the oil. Of course oils with a low vapour pressure and a low rate of decomposition must be used. A great improvement in the pressure level was obtained quite a long time ago by fractionation and by heating the condensed oil in the neighbourhood of the connection to the backing pump. Dissolved products were here removed from the fluid and pumped away.

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Recent experiments by Huber and Trendelenburg[7] and by Haefer[8] with an apparatus which could only partly be baked showed that pressures of about 10^{-9} Torr (equivalent nitrogen pressure) were obtainable without the use of liquid nitrogen. Huber and Trendelenburg used a special bakeable baffle. Haefer got this pressure at the end of a glass tube which had been thoroughly baked. Both investigators found that after a hundred to a few hundred hours the pressure started to rise. Haefer explained this by assuming a non-steady flow of oil vapour through the glass tube where the sticking time is very great. Consequently, conditions of steady flow are not attained until a very long transition time has elapsed. Obviously one has to work in the direction of large area adsorbers as it has been done in this country by Biondi[9] with zeolite and aluminium oxide.

Also Powmer has described an all-metal ion system with an oil diffusion pump in which even a pressure below 10^{-10} Torr has been achieved without the use of liquid nitrogen[9a]. The pump fluid used was Silicone 704.

Using liquid nitrogen traps in combination with their oil diffusion pump Amoignon and Moreau[9b] succeeded in obtaining pressures as low as some 10^{-10} Torr.

(b) *Getter-ion pumps*

Herb's work on titanium ion pumps has been continued at various places in Europe.

In these getter-ion pumps titanium is generally used to getter all chemically active gases, while the inactive gases are ionized, removed by an electric field and collected on the walls or on electrodes.

Investigations into large-capacity pumps have been reported from England, Russia, Germany and France.

Holland, Laurenson and Holden[10] and also Winogradoff[11] used bombardment by electrons to heat and evaporate the titanium, Reich and Nöller[12] and also Kienel and Lorenz[13] employed resistive heating.

The main interest of investigators working on tube technology has lain in the direction of small pumps which could be used for special tube pumping or during ageing. The ion pump may be kept attached to the tube when this is in full operation with all the tensions applied. When gas evolution has dropped sufficiently the ion pump can be removed.

In this connection the work of Klopfer and Ermrich[13], of Huber and Mrs. Warnecke[14], of Robinson[14a], of Pressel[15] and of Smith[16] must be mentioned. Klopfer and Ermrich not only designed a simple titanium pump with a Penning discharge, but also studied the circumstances under which very low pressures can be obtained with titanium-ion pumps. They pointed out that it is necessary to degas the pump itself by heat treatment, as is the practice with mercury diffusion pumps. An ion pump with a great pump speed is also effective because methane is formed on the getter mirror and this is not chemically combined. Continuous evaporation is only of value when the starting material has been thoroughly degassed, as otherwise a considerable amount of hydrogen and methane may be produced, which raises the residual pressure. If all the necessary precautions are taken pressures in the 10^{-10} Torr region can certainly be obtained. We have used the pump designed by Klopfer and Ermrich[17] for pumping special tubes like travelling wave tubes, magnetrons, klystrons and power transmitting tubes, always with great success.

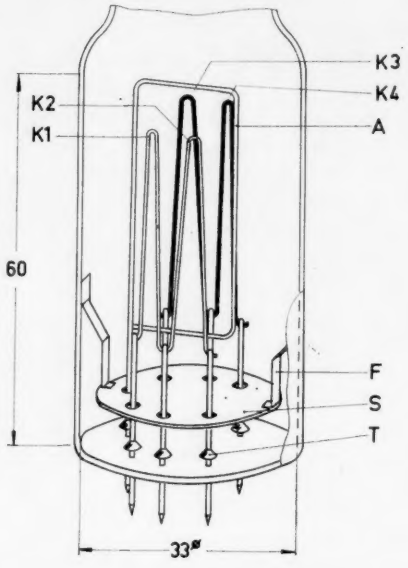

FIG. 2. Titanium-ion pump with a Penning discharge, and with four hot cathodes.

A, anode ; K_1, K_2, K_3, K_4 cathodes ; S, T, metal screens.
F, connection with evaporated layer.

The version designed by Huber and Mrs. Warnecke[14] does not employ a Penning discharge but has a triode or tetrode system in which the anode supplies the titanium and is heated by electron bombardment. As the authors state these pumps have also been used successfully in the evacuation of ultra-high frequency tubes.[18]

So far no published information is available on the use of the Hall version[19] of the titanium ion pump. Dr. Klopfer who has experimented with this type of pump considers it quite promising[20].

3. Gas analysis

I propose to limit myself to those instruments for gas analysis which are suitable for determining gas compositions in electron tubes ; obviously, then, I shall not have to deal with any of the large instruments. The first requirement for a mass spectrometer to serve this purpose is that it should not influence the gas composition to any but a negligible extent. This means in the first place that it has to be very small and further that it must be possible to degas it thoroughly. Most attention has been given to the omegatron[20a], other spectrometers which have been used are of the Bennett type[21] and the Farvitron[22].

The use of the Bennett spectrometer is mentioned by Warnecke[23]. It consists essentially, as you will know, of an array of grids that create r.f. fields in which ions of a certain charge e and mass m undergo successive accelerations. It is possible to collect these ions at the end of the tube and

identify them in virtue of the relationship between this charge e and mass m, the characteristics of the field and the geometry of the instrument. Besides the absence of a magnet, its main advantage over the omegatron is its capacity to measure higher gas pressures, with a limit of about 5.10^{-4} Torr.

The Farvitron, invented by Tretner[23] is an electrostatic mass spectroscope. In this device ions, formed by an electron beam, travel to and fro in a tube, being repelled at both ends by an electrostatic field. The frequency of these oscillations depends on the mass and the charge of the ions. By modulating the ionizing electron beam in the same frequency as that of a particular ion oscillation, clouds of these ions are formed which travel just in phase with earlier formed ions of the same kind, resulting in an increase of the induced current in the end electrodes. Induced currents from ions with different mass, oscillating at another frequency undergo no increase. By sweeping the modulating frequency over a range of frequencies such that in principle masses from 1 to 300 can be recorded—the sweep frequency can be that of the mains supply—a continuous record of the complete gas composition is obtained. The device operates well between 10^{-8} Torr and 10^{-5} Torr, the resolving power being about 20. Reich and Flecken[24] have reported some results obtained with this spectroscope. It cannot be used for accurate measurements but it is simple, it operates quickly and is thus suitable for monitoring work.

The omegatron has been used for gas analysis by various investigators among whom I would mention Reich and Nöller[25], Klopfer, Garbe, Schmidt[26–28], Francken and van der Waal[29], Baker and Giorgi[30]. Although I may assume that you are all familiar with the omegatron I will very briefly recall the way it functions. A beam of electrons of sufficient energy travels along the lines of a homogeneous magnetic field. The ions formed by the beam will move spirally in this field. The angular frequency depends only on the magnetic field and the e/m ratio. By applying a r.f. electric field perpendicular to the magnetic field ions of a particular e/m value will be accelerated at the right instants so that their orbits will grow steadily. These ions are in resonance and they can be collected at an electrode somewhere on the periphery. Ions with a different e/m ratio will not be in resonance and their orbits will grow and shrink regularly, so they do not reach the collector. By varying the r.f. frequency a mass spectrum can be obtained. The original version of the omegatron did not allow gas compositions to be deduced correctly from ion current values because these were not strictly proportional to the ionization cross section. The collector only captures some of the ions present in this instrument having a given e/m ratio, and the proportion reaching the collector is different for different ions. Now Klopfer[31] has succeeded in making an instrument in which every ion formed reaches its collector, apart from those that have collided with molecules, and which provides for every gas present, a reading that is proportional to the ionization cross-section. It is therefore possible with this omegatron to calculate the ion current which will be found at a certain pressure and with a certain electron current, provided the ionization cross-section is known. This result has been achieved by adding two side plates close to the guard rings in the original design by Sommer, Thomas and Hipple. These side plates are given a negative potential with respect to the upper and lower plate between which a r.f. voltage is applied. An electrostatic field is thus produced in the omegatron which forces the ions along electrostatic potential lines in the direction of the ion collector, which is placed in the lower plate. The result is that all ions which have not collided with molecules reach the ion collector. Really quantitative measurements are now possible in the pressure range of 10^{-5} to, say, 10^{-12} Torr, the upper limit being determined by losses due to collisions with the molecules, to lower limit by the amplifier, which has in this case a sensitivity of 10^{-16} A. The resolving power amounts to 40 with a magnet of 5000 Gauss.

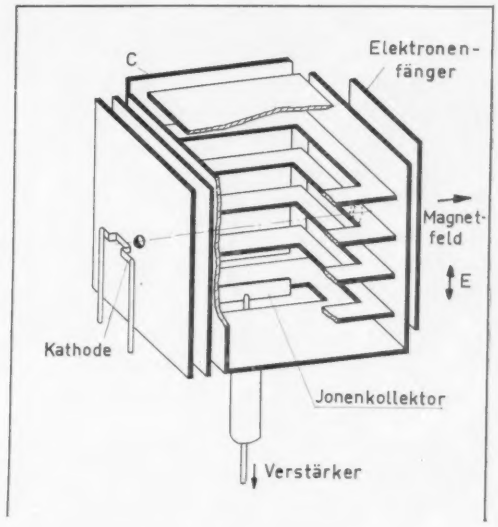

FIG. 3. The Omegatron with side plates.

With this instrument numerous analyses have been made in the last few years on different kinds of vacuum systems. Some of the studies originating in this work are worthy of mention here. In their paper on the influence of gas reactions in vacuum systems on the composition of the residual gas, Baronetzky and Klopfer[32] considered the production of carbon monoxide and hydrogen by the reaction of water vapour on tungsten carbide or carbon. Such a reaction practically always occurs when a hot tungsten filament is used, as very small amounts of water vapour and of carbon are almost always present. In equilibrium this reaction lies completely on the CO and H_2 side in the circumstances encountered in normal practice. They further investigated the thermal decomposition of methane, a gas mostly found in getter containing systems. Although at slightly elevated temperatures a decomposition could be expected thermodynamically, it has been observed with the omegatron that the reaction rate is so small that hardly any decomposition takes place at an oxide cathode surface with a temperature of 800°C. On a tungsten surface at 1900°C however the decomposition is quite appreciable, the pressure dropping

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to half its original value in 5 min in a volume of 1 l. and with a tungsten area of 0.1 cm^2. I mention these effects, perhaps somewhat superfluously, because I believe that one must be quite aware of them in interpreting gas analysis results.

Klopfer, Garbe and Schmidt[27] succeeded in working out a general scheme of classification for residual gas composition in vacuum systems such as radio valves, TV picture tubes and ultra-high vacuum systems consisting of glass or of glass and metal. I will end my survey on gas analysis with special reference to electron tubes by discussing their paper in some detail. The systems for which such a general scheme can be made must satisfy a number of conditions :

(a) The system may only contain materials which are commonly used in the manufacture of ultra-high vacuum systems and electron tubes.

(b) The vapour pressure of the materials used must be negligible at the prevailing temperatures.

(c) The permeation of gases through the walls from the surrounding atmosphere should not contribute to the amount of gas given off by the sealed-off system.

(d) In gettered systems the getter should not become exhausted during the lifetime of the system.

(e) The previous history of the system, i.e. all previous treatments such as degassing and pumping processes, must be fully known.

The gases most commonly evolved from the materials used in systems which meet these requirements are H_2, H_2O, N_2, CO, O_2 and CO_2. For example, H_2O and CO_2 may be evolved from the glass, and H_2 and N_2 from metals which have been treated in forming gas. Due to the interactions between the gas and the surfaces, which play a predominant part in the gas composition, a scheme with a few groups can be made, each with its own predictable residual gas composition. I will discuss the various gas surface reactions briefly :

(1) Adsorption on cold surfaces. H_2O and CO_2 which are released during baking are strongly readsorbed during cooling. They may react in the warm period with hot metals forming oxides and carbides. Also O_2 is bound to oxides and the gases left in a well baked system after cooling are H_2, N_2 and CO.

(2) Reactions between the gases and the getter. A barium getter reacts strongly with gases such as H_2, N_2, CO_2, CO and of course O_2 as long as it is unsaturated. In getter metals such as Ti, Zr and Ta the H_2 dissolves and the pressure is determined by the temperature and the amount taken up already. Very important is the reaction of H_2O with the carbide like constituents in the getter originating from a former reaction with CO[33]. In this way hydrocarbons are formed, CH_4, C_2H_6, C_3H_8. Also the presence of carbon and hydrogen in the getter material leads to the production of hydrocarbons during flashing. The result is that after flashing the getter the gas consists almost entirely of hydrocarbons. In non-degassed systems the H_2O pressure will predominate in the beginning, but later on the hydrocarbons determine the pressure.

(3) Reactions between the gas and the cathode. At the cathode the circumstances are very complicated, owing to the temperature differences. In this respect mention must be made of the gas evolved from the mica. The main gases given off are H_2O or CO, N_2 and H_2. The thermal dissociation of CH_4 has been mentioned already. Hydrogen is also dissociated on a hot cathode, the atoms either being strongly adsorbed or giving rise to reaction products. Oxidizing gases will form CO with carbon impurities in the cathode. CO_2 has also been found to be formed on an oxide cathode or on a cathode of platinum–iridium covered with thoria, when H_2O or O_2 was present. At pressures of about 10^{-6} Torr the amounts of CO and CO_2 were of the same order of magnitude. Oxide cathodes and dispenser cathodes evaporate barium which may be converted to carbide which can react further to hydrocarbons.

(4) Effects of ion pumping. Here too the conditions are very complex. Besides the pumping action gas may be released by the electron or ion bombardment. Dissociation due to electron bombardment may occur. A decrease in noble gas content, as for argon, which is always found when barium getters are used, can only be achieved by ion pumping.

To sum up, these authors have arrived at the following conclusions about the gas composition under the various conditions. The gases are given in order of abundance.

(a) In a system with the cathode cold,
without a getter : H_2, N_2, CO, CH_4
with a getter : CH_4, C_2H_6, (A), C_2H_6, C_3H_8
with a getter and ion pump : H_2, (A), N_2,CH_4

(b) In a system with a cathode at 900–1200 °C,
without a getter : H_2, N_2, CH_4, CO
with a getter : H_2, CH_4, N_2, (A), CO
with a getter and ion pump : H_2, N_2, CH_4, (A), CO

(c) In a system with a cathode at 1500–2000 °C
without a getter : CO, N_2
with a getter : CH_4, (A), CO, N_2
with a getter and ion pump : CH_4, CO, N_2, (A).

4. Conclusion

I think my talk would be very incomplete if I did not mention a few other investigations and results which will be of interest to you. It is not however my intention to treat this work in detail.

First I will remind you of a new development in the field of mechanical pumps, viz. the molecular pump described by Becker[34]. You know that, so far, molecular pumps having the advantage of giving a " pure " vacuum without the use of traps have suffered from the problem of the very close mechanical tolerances, a problem which was difficult to solve. It has never been possible to employ this type of pump on a large scale. In the new construction much less severe demands are made on the dimensions of rotor and stator. These parts are composed of a number of disks. The rotating disks forming the complete rotor alternate with the stationary ones of the stator. The distance between successive disks is 1 mm, i.e. 20–30 times the distance between the rotor and stator of other molecular pumps. The pump action is obtained because the disks have oblique slits, the

gas being forced in one direction in the wedge-shaped channels thus formed. A pump speed of 140 l./sec is obtained while a pressure as low as 5.10^{-10} Torr has been achieved. I feel that applications are likely to be found not so much in tube technology as in mass spectrometer systems, accelerators and foundry equipment.

The last subject which I would like to mention is getters, a difficult subject and not only because the circumstances in which the getters are activated differ widely, which has of course its influence on their gettering properties. Most of the work has been done on barium getters, although van Vucht[35] made an elaborate study of the Ceto getter. The interest in non-evaporating getters is also evident from Sourdillon's[36] work on Zr and Ti. Hejzlar and Horáček[37] worked on " mischmetall " getters, a mixture of cerium and anthanum, with a view to obtaining a residual gas atmosphere rich in hydrogen.

Mention must be made of work on barium getters by Bloomer[38], della Porta and co-workers[39], and by Fransen and Perdijk[40]. It must be remarked that both the interior and the surface of a barium mirror are influenced by the gas present during evaporation. These gases are evolved from the getter components, from the surroundings, etc. Therefore the behaviour of a getter will differ in different cases, and this may result in a lack of agreement between various investigators. Bloomer and della Porta and co-workers have paid particular attention to diffusion mechanisms in and on the mirror. Perdijk has given attention to the structure of the mirror, showing that good layers, produced under circumstances met with in actual practice, consist of small globules with a diameter of about 0.05μ. If the substrate is kept too hot the globules sinter together and the quality of the layer becomes worse. These globules are not formed on the glass but escape in this form from the getter bar and Perdijk speaks therefore in this case of sputtering. Although our knowledge of getters has increased during the last few years we must confess that it is still very incomplete.

I must apologize for not having discussed other subjects belonging to vacuum technique, such as leak testing, manometers, seals etc. You will agree that time was too short to do that in a responsible way. I hope however that I have succeeded in giving you an impression of the valuable work on vacuum technique recently done in European laboratories.

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The Characterization of CerAlloy 400 Getter

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Introduction

In the past twenty years a number of attempts have been made to characterize getters as to speed, capacity, and ultimate pressure. Most of these techniques were either unique to a particular getter or vacuum system or so general as to be of little technical interest. Of all of the approaches, only two are in common use today. These methods may for convenience be classified as the isobaric[1] and the isovolumetric[2] approaches. Each of these methods has, for the most part, been used separately by various investigators even though it may be shown that the two methods are not mutually exclusive[3].

Although the isobaric and isovolumetric methods of measuring the gettering rate may be derived from the same equation defining gaseous effusion, they differ markedly in their interpretation and application. It is imperative that anyone interested in evaluating the data presented in the published literature understand the subtle differences between these two methods. It is concluded[3] that the proper characterization of a getter must take the results from both the constant pressure and constant volume measurements. Although the conclusions so derived are based on the theoretical treatment of an ideal getter, they are valid considerations and greatly aid the interpretation when applied to real, non-ideal getters.

In the present work, account is taken of the non-ideal conditions that prevail at the surface of the getter, and an equation is derived which satisfactorily characterizes the getter at elevated temperatures. Since the equation so derived is based on fundamental physical phenomena, the data may be more completely interpreted and provide considerable insight into the basic processes which limit the behavior of getters.

Rate limiting processes

In common with all kinetic processes, low pressure gettering is limited in rate by various mechanisms, depending upon the temperature. At very low temperatures an energy barrier exists at the surface of the solid which drastically limits the rate at which the reactive gases may be chemically bound at the getter surface. At somewhat higher temperatures this surface barrier is less restrictive and the diffusion of the gas through the solid to form solutions or compounds limits the gettering rate. When very high temperatures are reached, diffusion becomes less restrictive and effusion may begin to limit the pumping speed. The transition temperatures from one condition to the next are not sharply defined but depend primarily upon the relative energies of the various processes involved.

In general, efficient getters will not be limited by a surface barrier in their normal operating temperature range because the pumping speed would be much too slow. On the other hand, effusion limited gettering is not observable because the temperatures required to make the solid state diffusion constant sufficiently large are also sufficient to cause chemical compound dissociation and/or vaporization. As a consequence, the diffusion of the gases into the solid getter should be the limiting mechanism over the entire useful temperature range for a getter.

The diffusion of gases into the solid does not eliminate surface reactions from consideration. The diffusion process may take place through the permeable surface film, and the observed diffusion constant would be characteristic of the film and not of the bulk metal.

Diffusion limited gettering

Since diffusion limits the gettering rate at low pressures, it is not feasible to use the equations previously discussed which are based on an effusion limited process. It will, therefore, be necessary to derive a new set of rate equations which are characteristic of this particular mechanism.

Consider a spherical getter of radius r_0 contained in a closed system of volume V. We will assume that the particular gas-getter system may be characterized by a concentration independent diffusion constant, D, and that Fick's law applies. If we require that the concentration of gas in the solid, either dissolved or chemically combined, is zero at the beginning of the gettering process, then the initial conditions to be satisfied by the solution of the diffusion equation are :

$$c = 0 \text{ at } 0 < r < r_0 \text{ when } t = 0 \qquad (1)$$

where c is the gas concentration at position r in the sphere. Since gas is diffusing uniformly from all directions toward the center of the sphere, there can be no concentration gradient at the center. Thus, one of the boundary conditions to be satisfied is :

$$\frac{\partial c}{\partial r} = 0 \text{ at } r = 0 \qquad (2)$$

It is now necessary to assume that the surface of the getter is always in equilibrium with the gas phase. This assumption is easily justified by resorting to the kinetic theory of gases describing the effusion process at low pressures. Molecular

effusion theory states that the number of particles striking a unit area in unit time is given by

$$\frac{dn^*}{dt} = \tfrac{1}{4} n \bar{c} \tag{3}$$

where $\bar{c}$ is the average molecular speed. Since the effusion rate predicted by this equation is always at least an order of magnitude greater than the experimentally observed gettering rate, the surface must at all times be accepting only a small fraction of the molecules that strike it. As a consequence, the surface of the getter may be assumed to be in an equilibrium condition with respect to the gas phase. Using a partition coefficient, K, to describe this equilibrium condition, an additional boundary condition may be written :

$$c = KC = NKP/RT \text{ at } r = r_0 \text{ and } t < 0 \tag{4}$$

where C is the concentration of gas in the gas phase, N is Avogadro's number, R is the gas constant, and T is the absolute temperature.

If we assume that no gas accumulates irreversibly at the surface of the getter (mass conservation), we may specify an additional boundary condition which is a statement that all gas entering the surface of the getter from the gas phase also leaves the surface of the getter into the solid phase. Thus :

$$\frac{V}{4\pi r_0^2}\frac{dC}{dt} = D\frac{\partial c}{\partial r} \text{ at } r = r_0 \text{ and } t > 0 \tag{5}$$

Using an effective volume ratio, defined

$$S = 3V/4K\pi r_0^3 \tag{6}$$

the boundary condition may be written in terms of the solid concentration.

$$\frac{Sr_0}{3}\frac{\partial c}{\partial t} = D\frac{\partial c}{\partial r} \text{ at } r = r_0 \text{ and } t > 0 \tag{7}$$

Solutions for the partial differential equation for diffusion subject to the initial and boundary conditions as specified above have been given by Carslaw and Jaeger[4], Wagner[5], and Wilson[6]. Because of the complexity of the solution which is in the form of an infinite summation, the various authors have written solutions in a form most suitable for their purposes. For the case describing the action of getters the solution obtained by Carmen and Haul[7] seems best, and in a modified form may be written

$$\frac{P - P_f}{P_0 - P_f} = \sum_{n=1}^{\infty} \frac{6S(1-S)}{9(1-S) - S^2 q_n^2} \exp(-q_n^2 Dt/r_0^2) \tag{8}$$

where P_0 is the initial pressure of the system, P is the pressure at any time, t, P_f is the final pressure of the system at infinite time, and the q_n terms are solutions, positive and non-zero of the equation

$$\tan q = 3q/(3 - Sq) \tag{9}$$

Since the solutions to the auxiliary equation increase in magnitude rapidly with n, the pressure solution at long elapsed times requires only a single term. Thus :

$$\frac{P - P_f}{P_0 - P_f} = \frac{6S(1-S)}{9(1-S) - S^2 q^2} \exp(-q_1^2 Dt/r_0^2) \text{ (large } t) \tag{10}$$

Diffusion limited gettering of hydrogen

The CerAlloy 400 getter pellet to be evaluated was placed in a vacuum system and heated to a temperature of 600°C. When the 0.4 cm radius pellet reached a stable temperature the 2.5 l. system was filled with hydrogen to a pressure of 9.5×10^{-3} mmHg. The pressure in the closed system dropped to a pressure of 2.1×10^{-6} in approximately 20 min as shown by the experimental points plotted in Fig. 1. It

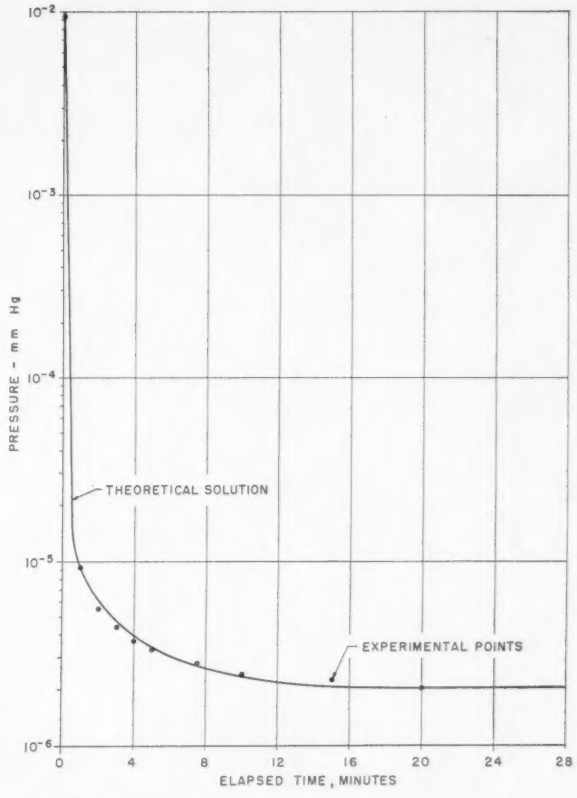

FIG. 1. Comparison of the experimental data with the theoretical solution for the adsorption of hydrogen on CerAlloy 400 at 600°C.

is now possible to evaluate the magnitude of the effective volume ratio and the diffusion constant for hydrogen at 600°C from this experimental data.

Taking advantage of the large time decay of the complete solution to a simple exponential, the extrapolated zero time intercept of the experimental data, Fig. 2, was used to determine the magnitude of the coefficient, which, with the calculated effective volume ratio, results in the value of the partition coefficient. A value of K of 1.31×10^7 was calculated from this data which indicates that the concentration of hydrogen at the surface of the getter under these conditions is about 10^{20} atoms/cm^3 or about 1 per cent. The slope of the exponential may be used to calculate the diffusion constant of hydrogen in CerAlloy 400 under these conditions. The results are in good agreement with the diffusion constants given by Barrer[8] for hydrogen at 600°C into palladium, nickel, and iron :

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D(Pd) = 3.15×10^{-4} cm²/sec.
D(Ni) = 1.42×10^{-5} cm²/sec.
D(CA 400) = 3.29×10^{-5} cm²/sec.
D(Fe) = 8.25×10^{-5} cm²/sec.

Having determined all of the important constants which characterize the rate processes, it is now possible to regenerate

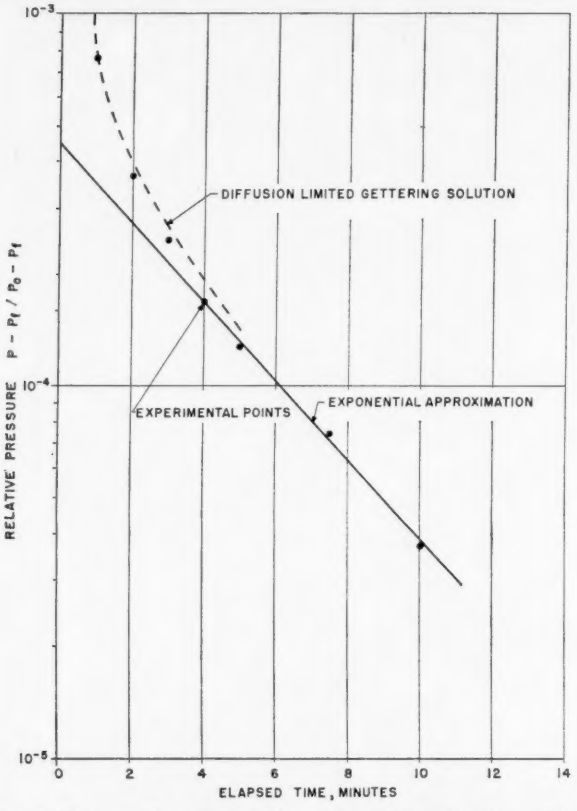
RELATIVE PRESSURE P - Pf / Po - Pf
DIFFUSION LIMITED GETTERING SOLUTION
EXPERIMENTAL POINTS
EXPONENTIAL APPROXIMATION
ELAPSED TIME, MINUTES

FIG. 2. The zero time extrapolation used to determine the partition coefficient and diffusion constant of hydrogen in CerAlloy 400 at 600 °C.

from the complete solution the pressure time curve shown in Fig. 1. To do this requires that a number of terms in the summation be evaluated, depending upon the magnitude of the elapsed time. The agreement again appears to be satisfactory.

Diffusion limited gettering of various active gases

The gettering of a number of active gases has been examined under a variety of experimental conditions. These gases include air, carbon dioxide, methane, oxygen, nitrogen, carbon monoxide, and hydrogen. Although the getter examined was very active with respect to all of these gases, the technique for describing the gettering behavior was developed only recently and not all of the information accumulated may be interpreted because of the lack of experimental control or properly defined conditions. For this reason, we will discuss only the quantitative behavior of the getter at 600 °C in an atmosphere of hydrogen (treated above), carbon dioxide, and methane.

The pressure versus time data accumulated for carbon dioxide and methane at 600 °C are shown in Figs. 3 and 4

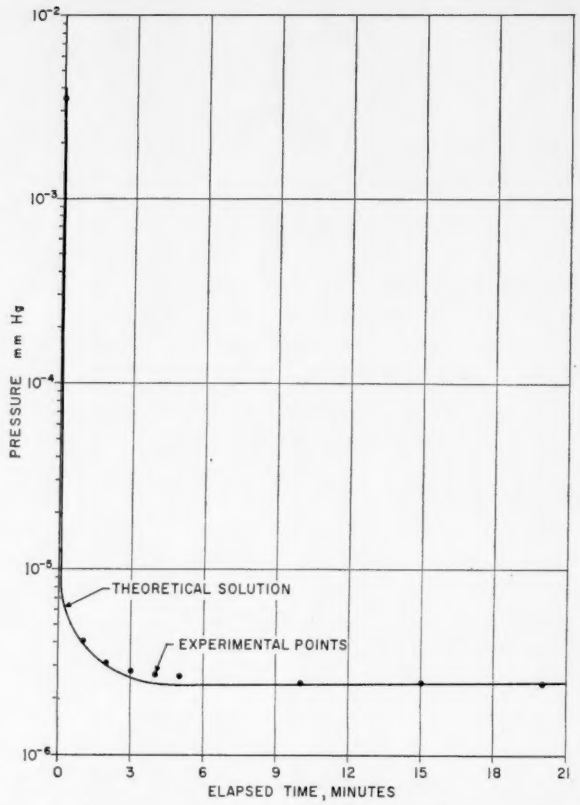

FIG. 3. Comparison of the experimental data with the theoretical solution for the adsorption of carbon dioxide on CerAlloy 400 at 600 °C.

and the corresponding zero time extrapolations for these gases are shown in Figs. 5 and 6. Performing the previously indicated calculations for the partition coefficient and the diffusion constant, the values given in Table I result :

TABLE I

Partition coefficient and diffusion constant for gases in CerAlloy 400 at 600 °C

Gas	Partition Coefficient	Diffusion Constant, cm²/sec
CH_4	4.5×10^5	1.3×10^{-5}
CO_2	2.2×10^7	4.0×10^{-5}
H_2	1.3×10^7	3.3×10^{-5}

Although the actual numbers that have resulted in this initial study have only limited significance, because of the structure sensitivity which will be discussed more fully below, the trends that persist are interesting and should be noted. The partition coefficient reflects the relative concentration of gas atoms at the surface of the getter. It is apparent from Table I that the concentration of CO_2 and H_2 are roughly comparable but that the concentration of methane is two orders of magnitude lower. This reduced concentration must therefore be responsible for the lower gettering rate observed for methane because the diffusion constant in this case is actually higher. Of the three gases, carbon dioxide is the

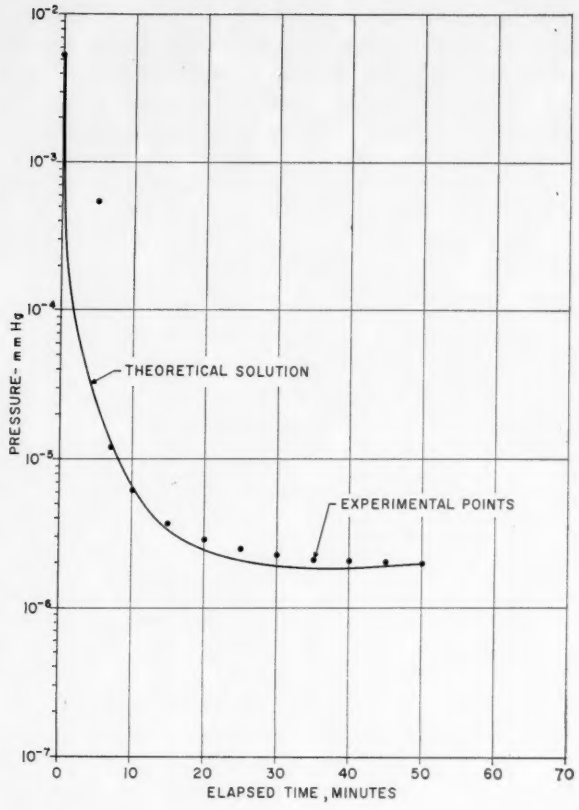

FIG. 4 (*left*). Comparison of the experimental data with the theoretical solution for the adsorption of methane on CerAlloy 400 at 600 °C.

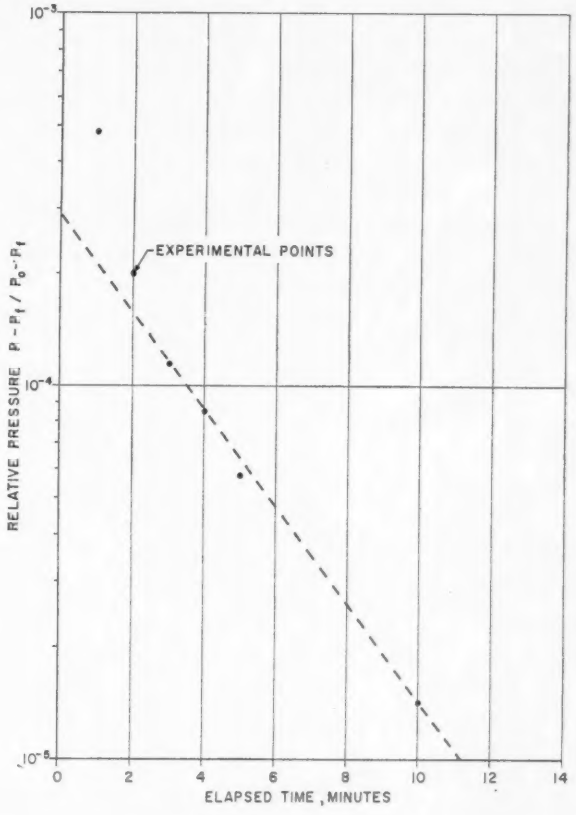

FIG. 5 (*above*). The zero time extrapolation used to determine the partition coefficient and diffusion constant of carbon dioxide in CerAlloy 400 at 600 °C.

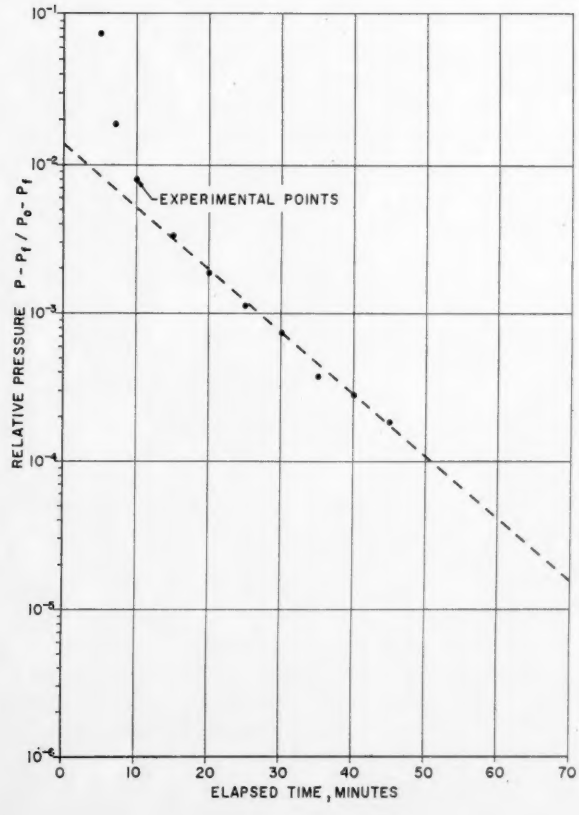

FIG. 6 (*left*). The zero time extrapolation used to determine the partition coefficient and diffusion constant of methane in CerAlloy 400 at 600 °C.

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most rapidly gettered by CerAlloy 400. This must be due to the fact that the surface concentration is highest. The lower gettering rate observed for hydrogen must be due primarily to the lower surface concentration, coupled with an intermediate diffusion constant.

If it is assumed that the process of gettering methane actually requires the consecutive processes of adsorption on the surface with subsequent decomposition to carbon and hydrogen, then the immediate question arises as to the small but significant differences between the diffusion constant of hydrogen and the apparent constant observed for methane. This may easily be accounted for by considering the fact that diffusion constants are seldom actually concentration independent, and that the concentration of hydrogen due to the methane decomposition would be two orders of magnitude lower than for the direct adsorption of hydrogen.

Effect of getter density on diffusion constant

In order to observe the effects of process variations on the diffusion constant, and to evaluate the true significance of the constants measured in this way, several parameters were varied in the getter preparation and the corresponding diffusion constants measured. One of the parameters of particular interest was the time the getter was sintered under normal processing conditions as this materially affects the grain size and density of the solid. In this series of experiments the getter was raised rapidly to sintering temperature in high vacuum. The sample was maintained at this temperature for the indicated time, cooled to 600°C, and the adsorption data taken. The zero time extrapolations for the adsorptions are shown in Fig. 7 and the calculated partition coefficients and diffusion constants are given in Table II.

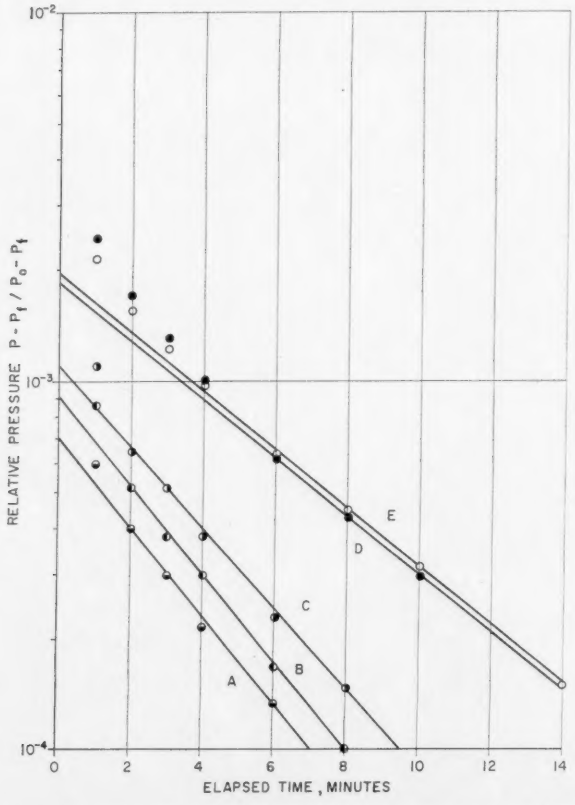

FIG. 7. The zero time extrapolations used to determine the partition coefficients and diffusion constants of carbon dioxide in CerAlloy 400 at 600°C as a function of sintering time. (A) 0 min ; (B) 30 min ; (C) 60 min ; (D) 120 min ; (E) 10 min at 100°C above normal sintering temperature.

TABLE II

Effect of sintering time on gettering of carbon dioxide at 600°C

Sinter, Time, min	Partition Coefficient	Diffusion Constant, cm^2/sec
0	8.85×10^6	3.64×10^{-5}
30	6.89×10^6	3.60×10^{-5}
60	5.64×10^6	3.30×10^{-5}
120	3.36×10^6	2.38×10^{-5}
120+	3.18×10^6	2.38×10^{-5}

It is of interest to note the correlation between the data presented above and the experimentally observed behavior of the getter in so far as gettering speed is concerned. Although the differences are not large, there is a definite decrease in the speed of the getter with increasing sintering time. This observation is in complete accord with the data presented in Table II which shows that the partition coefficients as well as the diffusion constants are reduced with increased sintering time.

Multiple adsorptions

In all of the above discussions, the data presented are for getters which were freshly prepared and exposed to the test gas for the first time. It is of interest, therefore, to consider some of the data collected where these conditions did not prevail and where multiple adsorptions were performed on the same sample.

In the first case the test sample was placed in a vacuum chamber and heated to 800°C for a period of 30 min while the chamber was being pumped. At the end of the 30 min bake, the chamber was isolated from the pumps and the sample temperature reduced to 500°C. The pressure in the system immediately dropped and was monitored as a function of time. After equilibrium conditions were established and the pressure had reached its lowest value, the sample was again heated to 800°C and the vacuum chamber opened to the pumps for a period of 30 min. The procedure was repeated a total of five times and the data accumulated plotted in Fig. 8. The composition of the residual gas adsorbed by the getter in these experiments is not known but presumably contains major quantities of nitrogen, oxygen, and water vapor.

The scattered data presented in Fig. 8 are the direct result of the temperature transient inherent in the test procedure, but collectively, the various data provide a reasonably good picture of the behavior of the getter. Using the procedures outlined above, the partition coefficient and diffusion constant for the residual gas are 6.21×10^3 and 6.1×10^{-5},

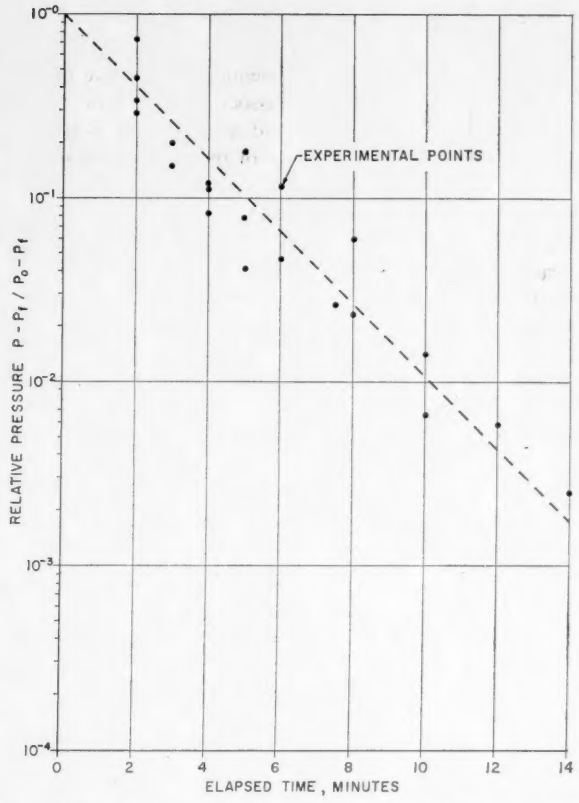

FIG. 8. The zero time extrapolation used to determine the partition coefficient and diffusion constant of residual gas on CerAlloy 400 at 500 °C after successive bakes at 800 °C.

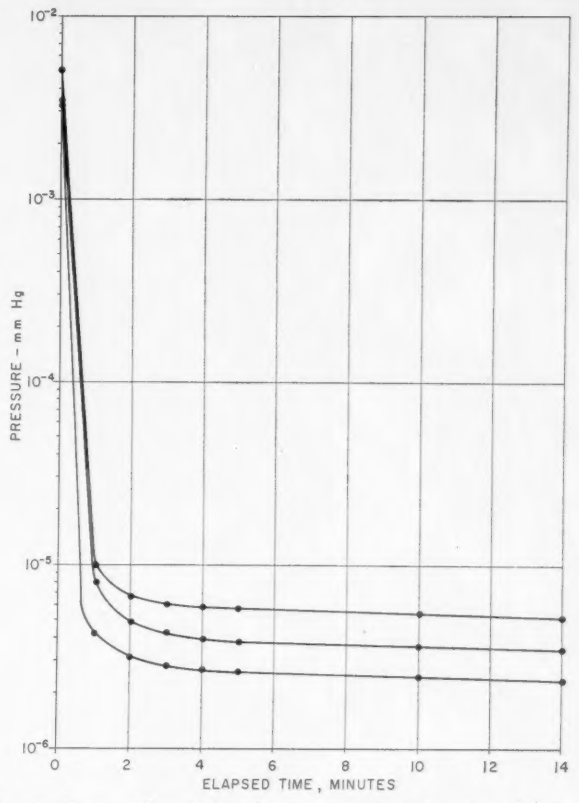

FIG. 9. The experimental data for the successive adsorption of carbon dioxide on CerAlloy 400 at 600 °C.

respectively. Note should be made of the fact that these data were taken for a sample at 500 °C, instead of at 600 °C, where all of the previous data were taken. This is presumably the reason for the lower partition coefficient and diffusion constant.

In the second case, the test sample was placed in the vacuum chamber and held at a temperature of 600 °C. The pressure in the system was then rapidly increased to 3.3×10^{-3} mmHg with CO_2 from an attached injection chamber. The pressure was then monitored as a function of time until a stable pressure was observed. A second injection was then made and the pressure in the system raised to 3.5×10^{-3} mmHg. The same procedure was followed through the third injection. The pressure data accumulated from these adsorption runs are shown in Fig. 9 and the collective zero time extrapolation shown in Fig. 10. Again there is some scatter in the data but the general form of the data is uniform. The partition coefficient and diffusion constant for this series of runs are 1.19×10^{7} and 4.68×10^{-5}.

Note should be made of the fact that each adsorption resulted in an equilibrium or final pressure which was higher than each preceding adsorption run. This behavior is not due to the fact that the getter is being depleted but rather reflects the adsorption-desorption which necessarily occurs on the vacuum chamber walls. Under normal conditions the system is pumped, without baking, until the pressure falls to the 10^{-7} mmHg range. When the test gas is then admitted to pressures in excess of 10^{-3} mmHg, adsorption on the chamber walls will occur, the amount adsorbed depending upon the contact time. The gas adsorbed on these surfaces will be gradually desorbed as the getter reduces the pressure in the system, the rate of desorption being determined by the amount of gas actually adsorbed on the walls. As a consequence, an apparent equilibrium condition persists when the getter adsorption rate exactly equals the desorption rate, which in turn increases with each successive injection.

Heterogeneous chemical equilibria

When a continuous bulk getter sorbs large quantities of gas, either one or both of two fundamental processes must be occurring. That is, either the gas is dissolving in the metal and forming a uniform solid solution, or it is combining chemically to form a stable chemical compound. In the case where a pure solution is being formed in the absence of any chemical combination or compound formation, then the laws governing dilute solutions should apply. In particular, we are interested in Henry's law for dilute solutions which specifies that the partial pressure of the dissolved component above the solution should be proportional to the mole fraction of the dissolved component in the solution. This may be written :

$$P = H(T)\,Xg \qquad (11)$$

where P is the partial pressure of the gas or dissolved component, X_g is the mole fraction of the dissolved component

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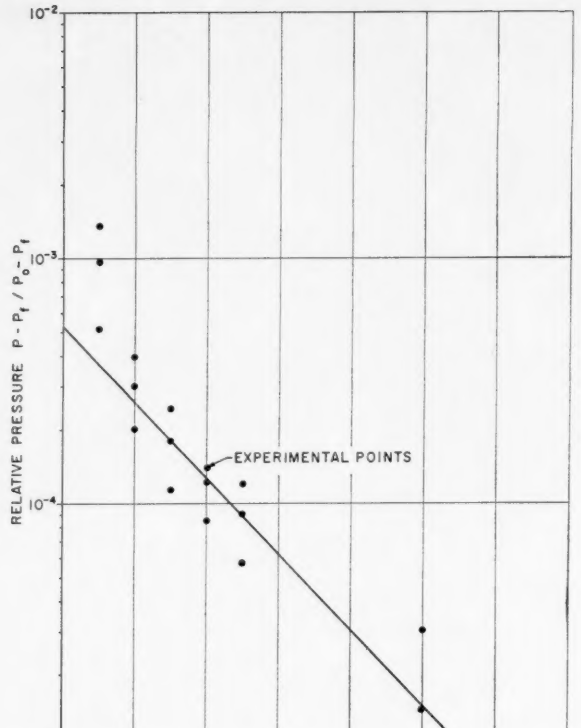

FIG. 10. The zero time extrapolation used to determine the partition coefficient and diffusion constant of carbon dioxide in successive adsorptions on CerAlloy 400 at 600°C.

in solution, and $H(T)$ is a temperature dependent proportionality constant determined by the heat of solution. From this relationship, were it applicable to the case of continuous getters, we would expect that the system pressure would increase linearly in proportion to the quantity of gas actually dissolved at constant temperature. In practice, this dependence is not observed, and the measured equilibrium pressure remains essentially constant over most of its useful life. We must conclude, therefore, that gettering in these materials must involve some form of chemical reaction, the other alternative mechanism.

Actually, the formation of chemical compounds must occur for other reasons. Most continuous gettering materials are pyrophoric in their useful temperature range, and the amount of energy released during their reaction even at low pressures is much more than can be accounted for by a heat of solution. In addition, the quantity of gas sorbed by these getters even at very low pressures is as high as several atomic per cent.

If we eliminate simple solution formation and consider only chemical combination as a mechanism for the normal gettering process, we arrive at a much more satisfactory explanation. In this case we must consider the rules governing heterogeneous chemical equilibrium. We are in particular interested in the thermodynamic conditions for equilibrium which specify that the chemical potentials of solid phases are constant at constant temperature and external pressure. This statement is equivalent to saying that the partial pressure of a substance is independent of the quantity of the substance present. Partial pressures are dependent only on temperature.

As a consequence, of the above considerations, it follows that the dissociation pressure of a solid compound into another solid and a gas phase will depend only upon the temperature of the system and not upon the quantity of the two solids present. This statement is true as long as some of each of the two solids are present and equilibrium is established. If we assume that the sorption of gas by a getter results in a homogeneous chemical compound, then the final pressure of the system will be determined only by the temperature and not by the amount of getter present or the amount of gas previously sorbed.

If these considerations are assumed to apply to the continuous gettering process, the dependence of the final pressure on temperature may be determined from chemical thermodynamic considerations. For a system involving gases at low pressure, the standard free energy change may be expressed in terms of pressure where the standard state is taken as the ideal gas at one atmosphere. As a consequence, the equilibrium constant for a single gas-solid reaction is just the partial pressure of the gas.

From the van't Hoff equation relating the variation with temperature of the equilibrium constant in terms of the change in heat content for the reaction, we may write

$$\frac{\mathrm{d}\ \ln\ P}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{12}$$

where ΔH is the change in heat content of the reaction at constant pressure. In order to perform an exact integration for Eq. (12) it is necessary to know the dependence of the heat content on temperature. This is generally not known, and the usual practice is to assume the ΔH is constant over limited temperature ranges so that the integration can be performed directly. Thus

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{13}$$

which for convenience in getter evaluation may be written

$$P = P_k e^{-\Delta H/RT} \tag{14}$$

where the values of the constants may be determined experimentally by observing the temperature dependence of the final pressure.

It is worth noting that Eq. (14) is only a convenience in comparing the properties of getters and should not be overinterpreted. Using the Nernst Approximation Formula for the integrated form of the Clapeyron-Clausius equation describing the single component dissociation pressures of compounds, we may write

$$\ln P = -\frac{\Delta H}{RT} + \sum 1.75\, n \ln T + \sum 2.3\, I n - 6.63 \tag{15}$$

where I is known as the Conventional Chemical Constant and n refers to the mole balance of the reaction. Since the values determined by Nernst for all gases fall between 1.5 and 4.0 and are well defined, it should in principle be possible to calculate the final pressure over a getter using only Eq. (15) and the known values of the constants. Values of I between -5 and -10 are required for continuous getters.

The fact that negative values of the Conventional Chemical Constants are required to explain the data is quite interesting and leads immediately to a clue to the mechanism of gettering. The inferred negative values of I from Eq. (15) indicate that $\ln T$ and I terms are too heavily weighted and that values of n less than unity are required. This is in agreement with the postulation that a solid solution reaction instead of a stoichiometric reaction is responsible for the observed gettering action.

The heat content and dissociation pressure

As was stated previously, the final pressure in an ideal gettered system will be dependent only upon the dissociation pressure of the compound formed, regardless of the composition of the compound. Because of the solid solution formed, we may express the final pressure in terms of the heat content and a proportionality constant, P_k, which must be determined experimentally. Figure 11 shows a plot of the

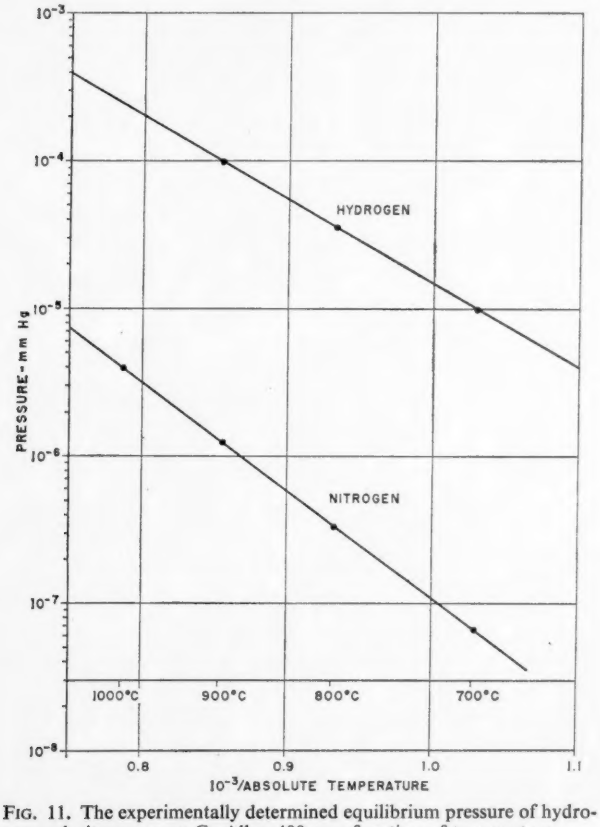

FIG. 11. The experimentally determined equilibrium pressure of hydrogen and nitrogen over CerAlloy 400 as a function of temperature.

logarithm of the final pressure versus $1/T$ for the two gases, nitrogen and hydrogen. The high temperatures for which the data were taken were necessary to avoid a leak-limited pressure as discussed below.

The data plotted in Fig. 11 illustrate a reasonably good correlation with the theoretical prediction and allow one to calculate the two constants necessary to characterize the getter for these two gases. Using Eq. (14) the heat contents for the two reactions may be calculated yielding 33,800 calories/mole for nitrogen and 26,200 calories/mole for hydrogen. In a similar manner, the values of P_k are 2.24 mmHg for nitrogen and 6.76 for hydrogen.

As a result of the above calculations based on the experimental observations we may write

$$P_f(\mathrm{N_2}) = 2.25\, e^{-33{,}800/RT} \tag{16}$$

and

$$P_f(\mathrm{H_2}) = 6.76\, e^{-26{,}2000/RT} \tag{17}$$

where P_f is the final pressure expressed in mmHg. A plot of Eqs. (16) and (17) over the useful low temperature range is given in Fig. 12. This illustrates the pressure that should

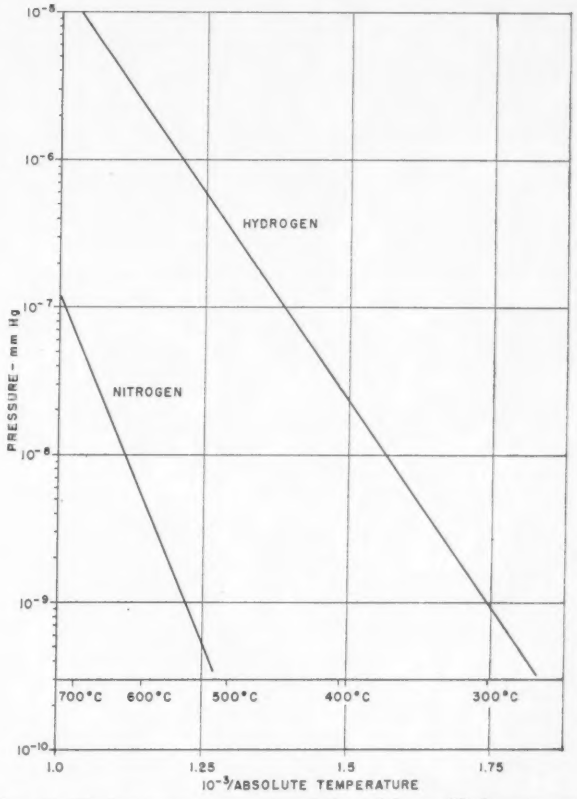

FIG. 12. The low temperature extrapolation of the equilibrium pressure of hydrogen and nitrogen over CerAlloy 400 as a function of temperature.

be achieved by the getter providing the system is leak free, and there is no degassing in the system.

These curves are of interest in other applications besides predicting the ultimate behavior of a system. Consider the getter to be at a temperature of 600°C in a system which is being evacuated. If the pump reduces the pressure in the system to 1×10^{-7} mmHg, then by an examination of Fig. 12, we can predict that hydrogen is being given off by the getter, and nitrogen is being adsorbed. If the temperature of the getter is reduced to 400°C, then both gases will be gettered under these conditions.

Virtual and real leak rate and the final pressure

In the previous discussions on the pressure that may be achieved by a continuous getter we assumed that the system

was ideal in that there were no real or even virtual leaks. For this case, it was found that the pressure at infinite time was determined only by the temperature of the system. Since no system is truly leak free, and since all components in a vacuum system tend to release dissolved gas, some consideration must be given to the final pressure that would be observed in such a real system.

Since it is impossible to specify beforehand the various leak rates and their dependence upon pressure, it is not possible to include such considerations directly in the pressure-time relationship derived earlier. Were these predictable, then a time dependent volume term could, at least in principle, account for the various leak rates in the derivation.

A reasonably accurate estimate of the equilibrium pressure in a leaking system may be made by taking advantage of the fact that the gettering action is diffusion limited. As a consequence, the gettering rate in a leaking system is exactly equal to the leak rate when the equilibrium pressure is attained. The state of the getter under these conditions is the same as that predicted by the original pressure-time equation (8), at the pressure P. It is possible, therefore, using Eq. (8), to calculate a time required to achieve a pressure P in an ideal system. Using this value of time in the differential rate equation, a gettering rate corresponding to this pressure may be calculated. The calculated gettering rate is equal in magnitude to the leak rate responsible for the steady state pressure P. If the probable leak rate is known beforehand, the reverse calculation will yield the probable value of the equilibrium pressure in steady state.

It is of interest to consider for a moment the influence that temperature might be expected to have on the final equilibrium pressure observed in a non-ideal system. Consider the case of a constant leak rate into a gettered system at very low temperatures. Since the diffusion rate decreases exponentially with decreasing temperature, the low temperature equilibrium pressure would be considerably above the calculated dissociation pressure. If the gettering rate is pressure independent and falls below the leak rate, the pressure will increase continuously until the pressure of the leak source is attained. As the temperature of the system is increased, the diffusion rate increases resulting in a lower observed equilibrium pressure. This trend of decreasing pressure will continue with increasing temperature until the dissociation pressure, which is increasing exponentially with temperature, becomes significant. As a consequence, further increases in temperature will result in exponential increases in equilibrium pressure. This general dependence of the equilibrium pressure on temperature at low temperatures is always observed experimentally.

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Specific Gas Reactions of CerAlloy 400 Getter Material

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1. Introduction

Although it is relatively simple to attain a high vacuum on a continuously pumping system if one uses conditions of moderate cleanliness, the maintenance of this necessary vacuum in a sealed-off tube presents a more difficult problem.

The subsequent evolution of gas from tube parts after pinch-off is probably the major source of gaseous contamination. There is a slow constant evolution into the closed system of the gases which have been sorbed by tube parts during or before bake-out and processing. Heating of surfaces after pinch-off for example, by bombardment of high energy beams, may cause a rapid evolution of gas.

Most clean metallic surfaces within a tube structure will clean up gas by surface adsorption at room temperature, and for many tube materials, e.g. tungsten, molybdenum and carbon, these gettering properties are increased at elevated temperatures. In addition, there are other mechanisms which result in gettering of residual gases. These include gettering achieved by positive ion bombardment of the cathode and other portions of the tube structure. Cathodes depending upon free barium and other active metals for emission also serve as gettering surfaces through chemical combination. These mechanisms, therefore, will normally getter gases that might evolve within a tube envelope during shelf life or under performance conditions. Thus, while some gas evolution will occur in tubes during operation or shelf life, surfaces within the tube structure will remove the free gas and maintain the high vacuum conditions necessary for operation.

However, extensive gas clean-up by cathodes or other surfaces can degrade tube performance and shorten tube life, e.g. through cathode poisoning or by increasing secondary emission ratios of electron bombarded surfaces. To prevent this type of contamination, it is often desirable to supplement tube part gettering with a specific getter material having a sufficiently high sorption rate and capacity to remove all residual and evolved gases. Another requirement is that the getter materials must not migrate, in order that there be no breakdown across insulators in the tube.

2. Description of CerAlloy 400

CerAlloy 400 getter material has many properties which make its application desirable in various vacuum devices. It is a coating type bulk getter with a very low vapor pressure at temperatures up to 800°C. Initial information on CerAlloy 400 was related primarily to its considerable reaction with carbon dioxide. The large quantity of carbon dioxide which is given off during conversion of oxide coated cathodes suggested the use of CerAlloy as a booster pump during this conversion. Interest in the detailed reactions of CerAlloy with other gases led to the program to be described.

CerAlloy 400 is a mixture of 80 per cent thorium, 5 per cent aluminum, and 15 per cent rare earth metals. The material can be purchased from Cerium Metals and Alloys Division of Ronson Metals Corporation in powdered form in a nitrocellulose, amyl acetate binder as well as in sintered pellet form or as a coating already bonded to base metals.

The sintering of CerAlloy 400 paste to nickel for these experiments was a reasonably simple operation. The parts to be coated were vacuum fired at 900°C–950°C for 45 min prior to coating. (Hydrogen firing the parts may also be used.) The paste should be applied uniformly to a coating weight of 20–30 mg/cm^2 as soon after vacuum firing as possible. The part should not be recoated or rapidly dried. Between the coating and vacuum sintering operations, excessive handling or vibration must be avoided. Coating and sintering should occur as soon after firing as possible. The part is sintered by heating it to 900°–950°C for 45 min in a high vacuum. The temperature of the part must be gradually raised. (Any rapid evolution of gas caused by a rapid rise in temperature will peel the coating.) During the sintering process, the vacuum should be as high as possible since a higher getter activity in tubes will result from higher vacua during sintering. Excessive heat in a gaseous atmosphere must be avoided after the CerAlloy has been sintered.

The getter chamber consists of a glass and nickel plated copper manifold, the getter assembly, a miniature thoria coated iridium filament ionization gauge made by W. R. & W. Scientific Glass Company (to minimize gauge pumping), knife edge seals, and two all-metal Granville Phillips vacuum

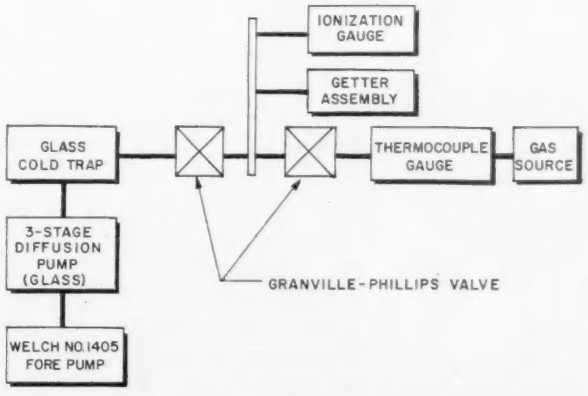

FIG. 1. Station diagram for getter analysis.

valves which isolate the manifold from the pumping system and the gas source independently. (See Figs. 1 and 2.) Encased in a glass bulb attached to the manifold, the getter assembly consists of a nickel cathode button assembly with an included heater. This assembly provides a convenient means of heating a CerAlloy coating uniformly. The button assembly is attached to an eight prong glass stem. A platinum platinum–rhodium thermocouple is used to measure the temperature of the CerAlloy. (See Fig. 3.)

Two types of gas introduction systems were used. The first means was a preferential diffusion of gases through metals, and the second was an injection from assayed reagent grade liter flasks of gas. Silver and palladium thimbles were used to introduce oxygen and hydrogen respectively into the system. The preferential diffusion of oxygen through

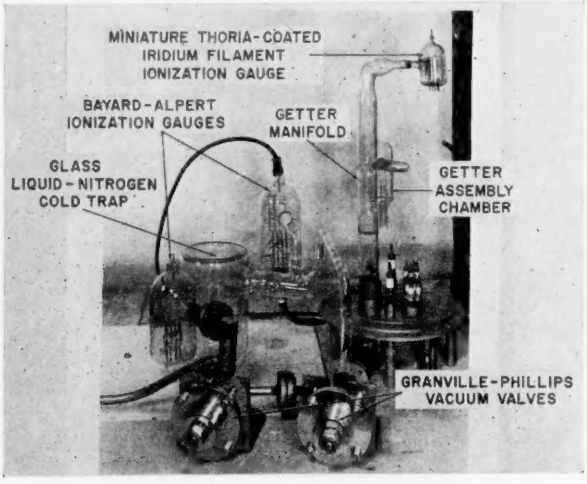

FIG. 2. CerAlloy 400 test manifold.

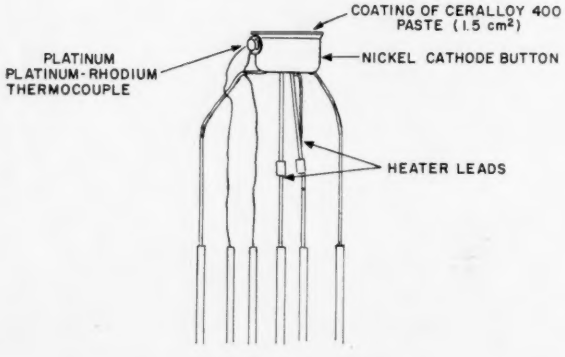

FIG. 3. Getter assembly.

silver enables one to obtain the pure gas in a simple manner. A helical nichrome heater was mounted around a metal thimble which had been brazed into a nickel sleeve. (The thimbles, which were 4 in. long, $\frac{3}{16}$ in. o.d. with a 0.050 in. wall, were purchased from Englehard Industries Incorporated, Baker Platinum Division.) Since the permeation and flow rates of gases through metals is dependent upon temperature as well as on the partial pressure of the gas outside the metal, the palladium thimble was heated in a forming gas atmosphere as a source of hydrogen. (The nichrome heater and thimble were surrounded by a heat shield and a small glass bell jar to permit the maintenance of a forming gas atmosphere around the palladium.) (See Fig. 4.) At 230°C, an appreciable flow of hydrogen (approximately 1.5μl./sec) was noted.

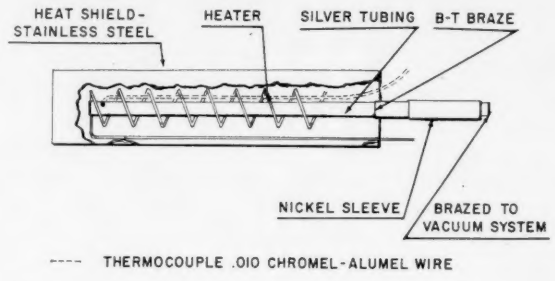

FIG. 4. Gas admission thimble.

The silver thimble was heated in air at 500°C. A leak rate of 20μl./hr of oxygen was observed. At temperatures above 500°C, the permeation and flow rates increase rapidly. The second method of gas introduction was the injection from assayed reagent grade liter flasks of gas. A glass manifold with glass gas flasks was used as a convenient gas source. A thermocouple gauge is used to measure the pressure between the glass stopcocks and the manifold inlet valve. (See Fig. 5.) Gases which are not available by the preferential

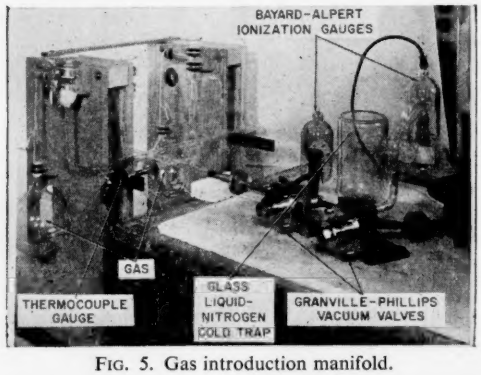

FIG. 5. Gas introduction manifold.

diffusion method and which are available in liter flasks are used in the glass manifold method. After the attainment of a clean system with a low ultimate pressure, methods of measuring the gettering characteristics of CerAlloy 400 had to be established.

3. Experimental methods

Two methods were used to measure the pumping speed and capacity of the gas-getter reactions. The static method is a means of introducing quantities of gas into a completely sealed non-pumping manifold. The entire system is first pumped down to its ultimate pressure, and the getter and ionization gauge grid are degassed. When this ultimate

pressure has been attained, the valves which isolate the manifold from the pumping system and the gas introduction system, respectively, are closed. The gas is allowed to enter the system up to the valve separating the manifold from the gas source. The getter is raised to the required temperature. The valve is opened and then closed to allow an amount of gas to enter the manifold. The quantity of gas introduced is established through reading pressure by the ionization gauge in the manifold, and the decrease is noted by a thermocouple gauge. The two quantities must, of course, be equal. The ionization gauge control panel has been modified to permit the grid voltage to be pulsed. One may, therefore, read the gauge with as little gauge ion pumping taking place as possible. After having been completely degassed, the getter will sorb a quantity of gas which has been introduced into the system with a definite initial pumping speed. The pumping speed of the getter will gradually decrease to zero at some specific ultimate pressure. If, however, additional gas is allowed to enter the system, CerAlloy will sorb the added gas. (See Fig. 6.) In the static method which was used for the present

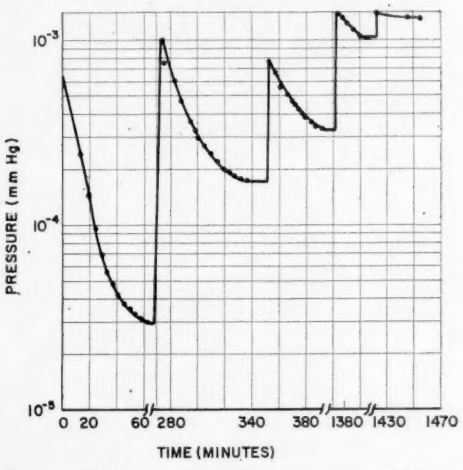

FIG. 6. Static method measurement of reactions of hydrogen with CerAlloy.

determination, the system was always filled to a specific pressure of gas (10^{-3} mmHg). In this case, the getter will sorb the additional gas at a lower pumping speed than the one measured after outgassing. The levelling pressure will be higher than the first ultimate pressure which is attained. After each addition of gas, the initial pumping speeds become respectively smaller, and the ultimate pressures become respectively higher until the rate of sorption is negligible (zero for all practical purposes). The getter is then filled to capacity at that pressure. (See Table I.) The initial pumping speed in liters per second can be calculated from the slope of the tangent to a pump down curve (See Fig. 6) of pressure versus time, dp/dt in mmHg/sec, at a specific pressure, P, from the equation :

$$S = -\frac{dp}{dt} \cdot \frac{V}{P} \qquad (1)$$

V is the volume of the system in liters. The static system method of calculating the capacity is simply that of multiplying the change in pressure (the pressure to which the system

TABLE I

Gettering of hydrogen by CerAlloy 400

Initial Pumping Speed, l./sec	Ultimate Pressure, mmHg	Gas Previously Gettered, μl./mg
1.26×10^{-3}	0.3×10^{-4}	—
0.91×10^{-3}	1.7×10^{-4}	0.026
0.22×10^{-3}	3.2×10^{-4}	0.058
0.17×10^{-3}	10×10^{-4}	0.074
—	13.5×10^{-4}	0.090

was filled minus the ultimate pressure) by the volume of the system for each successive addition of gas to the system. The capacity is the sum of these quantities of gas.

The dynamic method, which was the second method used to measure the pumping speed and capacity of the gas-getter reactions, is a means of permitting gas to leak into the system at a constant rate. After the getter and the ionization gauge are degassed, the entire system is evacuated to its ultimate pressure. Again, the valves which completely isolate the manifold are closed. Gas is allowed to leak into the manifold at a constant rate. The rise in pressure, dp/dt, in the system can easily be measured since the ionization gauge is continuously operated. The getter is raised to temperature. After a certain period of transition, a constant pressure is maintained. Again, the initial pumping speed may be calculated from Eq. (2).

$$S = dp/dt \quad V/P_{eq} \qquad (2)$$

where dp/dt is the change in pressure with respect to time due to the constant leak of gas into the system (which is determined before the getter is raised to temperature when no pumping is taking place), V is the volume of the system, and P_{eq} is the equilibrium pressure. However, as the pumping speed decreases, the levelling pressure (P_{eq}) increases. When the pumping speed has decreased to the extent that the levelling pressure has risen to a predetermined pressure, the getter is considered to be saturated at that pressure. Since a constant rate of gas evolution into the system dq/dt in μl./*sec*, is maintained for a definite period of time, the quantity of gas sorbed (the capacity in μl.) is known.

The method of investigating the outgassing characteristics of each gas from a saturated getter is fairly simple. After the getter has been saturated with the gas, the temperature of the getter is lowered to room temperature as the valve which isolates the gas source from the manifold is closed. The valve between the manifold and the pumping system is opened, and the system is evacuated. The grid of the ionization gauge is degassed. The manifold is again isolated from the pump system. The temperature of the getter is raised in equal temperature intervals of one hundred degrees each five minutes. The pressure of gas released at each temperature is pulse read on a miniature ionization gauge.

Both the static and dynamic methods of measuring the

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pumping speed and capacity characteristics of CerAlloy 400 have disadvantages. One disadvantage of the dynamic system is the fact that stability of parameters must be assumed. No reaction is eliminated. One attempts to measure the gettering effect which appears above the background. One must assume that background reactions, such as the pumping speed of the ionization gauge, do not change. It seems quite logical, however, that as the pressure in the system changes, reactions will take place which cannot be measured by a simple pressure determining device.

Several mechanisms (reactions of the gas with the filament of the ionization gauge and ion pumping of the gauge) interfered with the determination of the pumping speed and capacity of CerAlloy using the static method. Originally, a full-size Alpert type ionization gauge was used to measure the pressure in the system. Although the gauge was pulse read to eliminate ion pumping, the pumping speed of the thoria coated iridium filament for hydrogen is appreciable compared to the pumping speed of CerAlloy for hydrogen. In order to reduce the effect of gettering by the hot filament, a miniature ionization gauge with a tungsten filament was placed on the manifold. A flickering effect was observed to occur at pressures of 1–5 $\times$ 10^{-3} mmHg due to the combined effects of the cooling of the filament by the gas and the emission stabilizing control of the ionization gauge control panel. The dissociation of the gas in contact with the filament causes the adsorption of a large quantity of heat from the filament. The emission stabilizing control will attempt to maintain the cathode emission by increasing the power to the filament. This continuous raising and lowering of the filament temperature makes reading of the gauge almost impossible. To eliminate this disturbing effect, all measurements were taken at pressures low enough to reduce the obvious error in the determination of the pumping speed and capacity of CerAlloy 400 for various gases. One additional disadvantage of the static system is the fact that a great deal of time must be spent in determining the capacity of the getter. In order to keep the pressure low enough to avoid the variation in filament temperature previously mentioned, a small quantity of gas must be injected into the system. If the capacity of a reaction of approximately 100μl./mg is to be determined with a 20 mg coating sample, a total quantity of 2000μl. of gas must be sorbed. At single injections of 0.32μl., an exceedingly large number of injections has to be made.

4. Test data

Temperature has a definite effect upon the initial pumping speed of the getter. There is a definite temperature or range of temperatures at which the pumping speed of CerAlloy for a particular gas is greatest. (See Fig. 7.) The optimum initial pumping speed of all gas-getter combinations will not occur at the same temperature. A complete chart of the initial pumping speeds which have been determined so far may be seen in Table II. One may note the high pumping speed of CerAlloy 400 for carbon monoxide and carbon dioxide which originally suggested the investigation. The inversion that occurs in the oxygen mechanism may be explained. All of the rare earths form sesquioxides. When

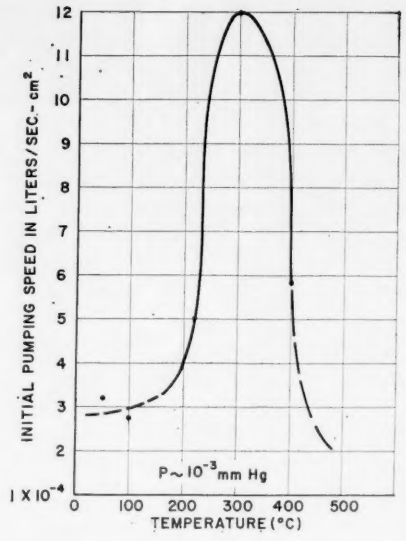

FIG. 7. Initial pumping speed of CerAlloy for hydrogen vs. temperature.

TABLE II

Initial pumping speed of CerAlloy 400 *getter material vs. temperature at approximately* 10^{-3} *mmHg*

Temperature, °C	Initial Pumping Speeds (in 10^{-4} l./sec) for a 1cm² area				
	Hydrogen	Oxygen	Carbon Monoxide	Carbon Dioxide	Nitrogen
200	3.0	30.7	4.47	.592	1.55
300	12.0				
400	5.8	30.0	534	2.97	43.0
600		8.1	30.9	139	68.3
900		10.3	1.07	3.28	

the rare earth metals are at elevated temperatures (in the presence of sufficient oxygen) cerium, praseodymium, and terbium form higher oxides. The sesquioxides tend to absorb water vapor. Surface oxide is converted into the hydroxide by water vapor. This hydroxide has a different crystal structure and increased volume ; it falls away from the metal exposing a fresh area for oxidation. The final result, which is the sum of the various mechanisms, is not necessarily a regular function. It is quite possible that the higher oxide formation results in a high pumping speed at 900°C.

The capacity of CerAlloy 400 (for each of the individual gases) also varies with temperature. However, the greatest initial pumping speed and the greatest capacity for each gas usually do not occur at the same temperature. Data which have been obtained thus far, on the capacities of CerAlloy 400 for various gases may be found in Table III.

TABLE III

Capacity of CerAlloy 400 *getter material vs. temperature at approximately* 10^{-3} *mmHg*

Temperature, °C	Capacity, μl./mg				
	Hydrogen	Oxygen	Carbon Monoxide	Carbon Dioxide	Nitrogen
200	3.25	1.18			.005
300					
400	.091	.122	1.10	2.20	.522
600		.292		89.0	.012
900		.091			

TABLE IV

Percentage of gas released from a saturated getter vs. temperature

Temperature, °C	Hydrogen	Oxygen	Carbon Monoxide	Carbon Dioxide	Nitrogen
200	0	0.8	.07	.27	.03
300	8	2.7	.10	.28	.04
400	23	4.2	.17	.31	.05
500	34	6.6	.68	.33	.08
600	41	8.0	.43	.47	.15
700	51	8.3	.43	.60	.23
800	81	8.0	.88	.97	.22
900	97	7.1	1.11	3.12	.39
1000	100				

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The outgassing characteristics (or the percentage of gas sorbed which is released) at any specific temperature does not seem to be dependent upon the temperature of the getter at which the gas was sorbed, nor upon the definite quantity of gas sorbed. There is a definite optimum temperature for the outgassing of a specific gas. Table IV shows the percentage of gas sorbed which is released versus temperature for each system. It should be noted that complete degassing or outgassing is generally not possible once the getter has sorbed certain gases. For example, the quantity of oxygen which the getter can be made to release is less than 9 per cent of that originally sorbed. In fact, the only gas which has a completely reversible reaction is hydrogen. The most efficient outgassing temperature for general degassing appears to be 900°C. The optimum gettering temperature which takes into account the initial pumping speed as well as the greatest capacity for each getter-gas combination lies between 300°C and 600°C at approximately 400°C.

5. Conclusion

The initial pumping speeds and capacities of CerAlloy 400 for individual gases have been determined. It has been shown to have excellent gettering properties for CO and CO_2 and moderate gettering for other common gases such as nitrogen, hydrogen, and oxygen. The outgassing characteristics (or the percentage of gas sorbed which is released) at any specific temperature have been measured. The reactions have been shown to be essentially irreversible except for that of hydrogen. The general gettering properties of CerAlloy 400 indicate many applications in vacuum devices.

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[2] B. Love; "Selection and Evaluation of Rare or Unusual Metals for Application to Advanced Weapons Systems", *Research Chemicals, Inc.*, Wright Air Development Center (June 1958).

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Degassing and Permeation of Gases in Tube Materials*

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Introduction

Because gases at low pressure are known to affect the performance of electron tubes, a knowledge of the gases evolving from the materials within the envelope and those permeating through the walls of the devices from external sources is therefore of importance in vacuum technique. These sources of gas are of particular significance in high-temperature vacuum devices. This paper describes a study of the degassing properties of materials, and the permeation of gases through materials considered important in the design of high-temperature, long-life microwave devices.

Measurement of permeation of gases through tube materials

Experimental method

The permeation of gases through tube materials involves the steady-state flow process from the gas phase on one side of the material to the gas phase on the other side. The metal samples used for permeation tests were in the form of seamless tubing approximately 20 in. long, having an outside diameter of $\frac{5}{16}$ in. and a wall thickness of 0.010 in. The ceramic samples were also in the form of extruded tubing having an outside diameter of $\frac{3}{8}$ in. and a wall thickness of 0.040 in.

After an initial degassing treatment intended to rid the test sample of internal gases, permeation tests were carried out at constant sample temperature. The evacuated sample tube was surrounded with the test gas at 1 atm pressure, while the inside volume of the sample was continuously pumped to maintain a high vacuum. Gases permeating through the sample were pumped away and analysed by means of the mass spectrometer.

The sample holder, shown in Fig. 1, consists of a tubular stainless-steel envelope having water-cooled copper end pieces which hold the smaller tubular sample to form a coaxial arrangement. The sample tube is sealed at one end to the gas-collection system, and its other end is sealed shut. Uniformity of temperature is achieved by means of stainless-steel disks inserted close to the water-cooled end pieces to make thermal contact with the sample tube and the inner wall of the envelope.

The stainless-steel envelope, the copper end pieces, and the tubular sample are soldered together with soft solder. The solder joints are all outside of the oven in the water-cooled region. Thus, a tight system is attained for the test gas, which flows through the envelope at one atmosphere pressure, at a rate of 1.5 ft^3/hr. Commercial tank gases were used for carbon monoxide, carbon dioxide and helium;

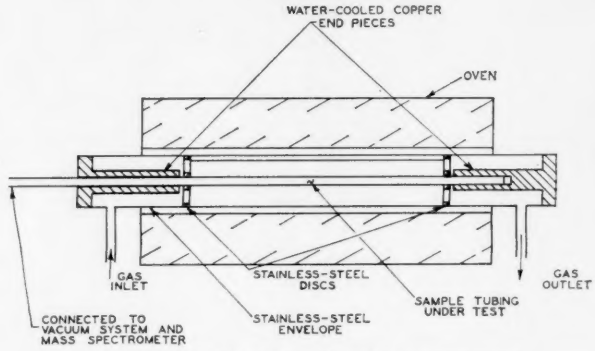

FIG. 1. Sample holder for permeation measurements.

nitrogen and hydrogen were obtained from plant gas lines. The test gas was passed through an Electrodryer to reduce water content and a dew point of less than −50°C was achieved.

The sample tube is closed by a metal plug brazed into one end; its other end protrudes through the copper end piece and is soldered to a Kovar tube which is sealed to the gas-collection system. The gas-collection system, shown in Fig. 2, consists of a mercury pump used to exhaust the sample

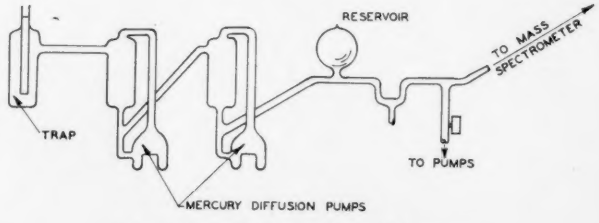

FIG. 2. Gas collection and analysis system.

tube, and a reservoir for the accumulation of gases for analysis in the mass spectrometer. In the present studies, a Model 21–620 mass spectrometer supplied by the Consolidated Electrodynamics Corporation was used.

Permeation measurements—metallic materials

Hydrogen.—After the initial degassing treatment, the permeation of hydrogen was determined at a constant

*Data presented in this paper were obtained under Air Force Contract No. AF 33(616)6563 on High Temperature Microwave Tube Design and Processing.

sample temperature. The gas quantities were collected and measured at intervals until a constant rate of permeation was achieved. The data on the permeation of hydrogen through Monel, Kovar, 52 Alloy, 304 stainless steel, Inconel, and nickel are shown graphically in Fig. 3.

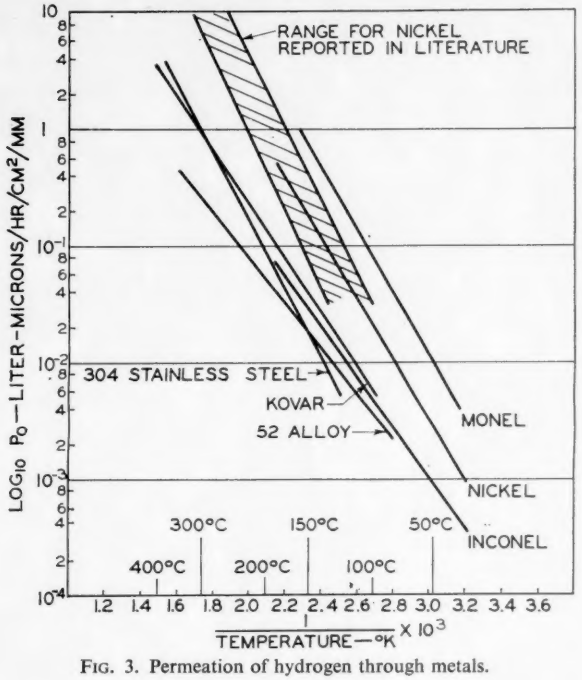

FIG. 3. Permeation of hydrogen through metals.

For the data on hydrogen, the permeation-rate constant P_0 is expressed as the amount of hydrogen, in l.μ, permeating 1 cm^2 of material, 1 mm thick, in 1 hr, when a pressure of hydrogen at 1 atm is maintained on the outside of the sample tube. Permeation of hydrogen through metals such as those studied here is assumed to follow the following relation described by Dushman[1] :

$$Q = P_0(AT\sqrt{P_{atm}})/a$$

where P_0 is the permeation-rate constant, and Q is the steady-state quantity of hydrogen permeating in time T through a sample of area A and thickness a with atmospheric pressure P_{atm} on one side, and a vacuum on the other side of the sample. In the present work, however, this dependence of Q upon sample thickness and hydrogen pressure was not verified, because the measurements were made at only one value of each of these variables.

Figure 3 shows the logarithm of the permeation-rate constant P_0 as a function of the reciprocal of absolute temperature. For all the metals studied, the data can be represented by a straight line in these plots. Therefore, the permeation rate is exponentially related to absolute temperature t by the equation

$$P_0 = A \exp(-Q/Rt)$$

where A is a constant, Q' is the activation energy, and R is the gas constant. The activation energies of the permeation process calculated from the slopes of the curves in Fig. 3 are given in Table I.

TABLE I

Activation energy data

Material	Activation Energy, cal/°K-mole
Monel	13,500
Stainless Steel	13,000
Inconel	10,700
Nickel	12,400
52 Alloy	9,200
Kovar	10,700

In the present work, hydrogen permeation in nickel was studied to obtain results of the measurement method for comparison with other investigations. The cross-hatched area of Fig. 3 represents the range of values of permeation-rate constants for hydrogen through nickel, calculated and reported by Dushman[1] from the published reports of five different experimenters. Present data agree well with previous data when compared in the overlapping range of temperature. Additional data on the permeation of hydrogen in nickel showing the same kind of agreement with this data have recently been published by Grimes[2].

Nitrogen, carbon monoxide, and helium.—The permeation of nitrogen and carbon monoxide was determined for the alloys Monel, Kovar, Inconel, 52 Alloy, and 304 stainless steel, at a sample temperature of 850°C. The measurements indicate no steady-state permeation of nitrogen, carbon monoxide, or helium ; the gas levels were independent of the compositions of gas maintained on the outside of the tubular sample. These levels, listed in Table II, thus represent a

TABLE II

Formation of carbon monoxide, nitrogen and helium

Material	Permeation-Rate Constant, P_0, l.μ/hr/cm^2/mm		
	Carbon Monoxide	Nitrogen	Helium
Inconel	0.00004	0.00004	0.000003
Monel	0.00004	0.00008	0.000003
Kovar	0.00002	0.00008	0.000003
52 Alloy	—	0.00006	0.00001
304 Stainless Steel	0.0004	0.0002	0.000003

persistent degassing of the sample and of that part of the collection system which is sealed off by the mercury cut-off during an accumulation period. Thus, permeation effects with these gases are small in comparison with the normal degassing rates of the materials tested.

Carbon dioxide.—The permeation of carbon dioxide in 304 stainless steel was determined at 750°C. The test apparatus was similar to that used for other metals, except that a glass envelope surrounding the tubular sample was used, and both ends of the sample protruded through the envelope to accommodate high-current leads for heating. Satisfactory uniformity of temperature was achieved over 12 in. length of sample (constant to within + 20°C).

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After the sample was initially degassed, two accumulation runs of four hours duration were made with carbon dioxide surrounding the sample. Because no effect on the ion peaks at mass 44 (CO_2^+) or at mass 28 (CO^+) was observed, the permeation-rate constant of carbon dioxide was thus found to be less than 0.00004 l.μ/hr/cm^2 area/mm thickness.

Permeation measurements—ceramic materials

The permeation of the ceramic materials forsterite and alumina was determined at a sample temperature of 750°C. The ceramic sample tube was mounted in the sample holder as shown in Fig. 1. Epoxy cement was used to close one end of the tube and to seal the other end to the gas-collection system. After a 15 hr degassing of the sample at 800°C in a helium atmosphere, extended permeation tests were made with hydrogen, nitrogen, carbon monoxide, carbon dioxide, helium, and air. In all cases, gas levels found were low and were independent of the composition of the gas on the outside of the sample. Permeation rates for all gases were lower than the background degassing levels of the sample and gas-collection system, consequently, the upper limits of the permeation-rate constants given in Table III are based on these background levels.

TABLE III

Permeation of gases through alumina and forsterite at 750°C

Material	Permeation Rate Constant, P_0, l.μ/hr/cm^2/mm					
	N_2	CO	CO_2	H_2	He	Air
Alumina	0.0003	0.00002	0.0002	0.00002	0.0002	0.0003
Forsterite	0.0003	0.00002	0.0002	0.00002	0.00002	0.0002

Measurement of thermal outgassing of tube materials

Experimental procedure

The seamless tubing used in the permeation studies was slit and opened to provide strips for the degassing tests having a thickness of 0.010 in. Before being degassed, the sample strips were degreased in ether, and washed in boiling deionized water and methanol. They were then gas- or vacuum-fired and mounted in an experimental tube. Vacuum- and dry-hydrogen (dew point −65°C) firing was carried out at 1000°C for 10 min ; plant-line hydrogen (dew point −35°C) firing was carried out at 900°C for 10 min.

The experimental tube is shown in Fig. 4. The metal sample, formed into a cylinder 1 in. *dia.* × $\frac{3}{8}$ in. height, is mounted on a nickel support structure which is attached to a tungsten lead stem. A chromel-alumel thermocouple (0.005 in. *dia.* wire) is welded to the inside of the cylinder $\frac{1}{8}$ in. from one edge for measurement and control of sample temperature. The sample is sealed inside a hard glass (Corning 7720) bulb and exhausted during a 1 hr oven bake at 400°C. After this process is completed, a mixture of solid CO_2 and acetone is placed around the cold traps so that a vacuum of 10^{-7} mmHg in the experimental tube can be attained. Gas evolved as a result of r.f. induction heating is then measured with a mass spectrometer. The heating and gas-accumulation schedule included two 10 min heating

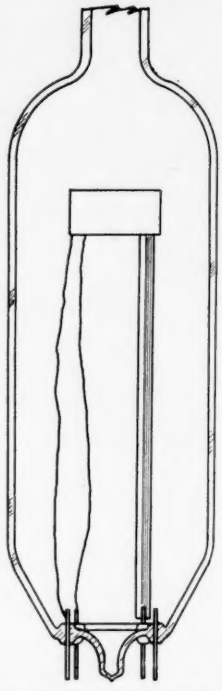

FIG. 4. Experimental tube.

steps to 600°C and two accumulations. Gases were similarly accumulated after each of two heatings to 800°C and two heatings to 1000°C.

Experimental results

403 *Monel.*—This material is a copper-nickel alloy having an approximate composition of 57 per cent nickel and 43 per cent copper. Average quantities of total gas evolved from this material when heated to 1000°C are listed in Table IV for various pretreatment methods. As shown, degreasing samples which were both degreased and fired in plant-line hydrogen desorbed substantially higher quantities of carbonaceous gases than did those processed by degreasing

TABLE IV

Degassing of 403 Monel

Pretreatment of Sample	Total Gas on Heating to 1000°C, l.μ/g		
	H_2	CO N_2*	CO_2
Degreased Only	2.8	21.0	2.9
Degreased and Line-Hydrogen-Fired	1.0	71.0	9.1
Degreased and Dry-Hydrogen-Fired	1.0	6.7	1.7
Degreased, Dry-Hydrogen-Fired and Vacuum-Fired	0.6	6.4	1.6

*Note : Nitrogen not determined separately from carbon monoxide, but is less than 10 per cent of the total.

alone. However, when the metal was degreased and dry-hydrogen-fired, significantly lower amounts of carbonaceous gases were obtained. A third set of values obtained from samples which were degreased, dry-hydrogen-fired, and vacuum-fired, gave no significant further decrease in the carbonaceous gases.

304 *Stainless steel.*—AISI type 304 stainless steel has an approximate composition of 0.08 per cent carbon (maximum), 18 to 20 per cent chromium, and 8 to 11 per cent nickel. Average quantities of total gas evolved from this metal when heated to 1000°C are listed in Table V for various pretreatment methods. Gas evolution from 304 stainless steel is greatly effected by the pretreatment method. Table V shows, for example, that samples which were both degreased and dry-hydrogen-fired desorbed significantly lower amounts of all gases, excepting carbon dioxide, than did samples which had been degreased only. When the material was dry-hydrogen-fired and vacuum-fired, a further significant reduction in evolved gas, especially nitrogen, was obtained. When the material was nickel-plated and dry-hydrogen-fired, nitrogen was even further reduced, leaving carbon monoxide as the principal gas component.

TABLE V

Degassing of 304 *stainless steel*

Pretreatment of Sample	Total Gas on Heating to 1000°C, l.μ/g			
	H_2	N_2	CO	CO_2
Degreased	5.1	86	30	0.8
Degreased and Dry-Hydrogen-Fired	1.6	67	12	0.9
Degreased, Dry-Hydrogen-Fired, and Vacuum-Fired	0.6	12	13	0.5
Nickel-Plated and Dry-Hydrogen-Fired	1.0	2	11	2.7

Other tube materials.—Average quantities of total gas evolved from various alloys when heated to 1000°C are listed in Table VI. The approximate compositions of these alloys are as follows :

Kovar
54 per cent iron, 28 per cent nickel, 18 per cent cobalt

Copper–Nickel
70 per cent nickel, 30 per cent copper

Inconel
80 per cent nickel, 15 per cent chromium, 5 per cent iron

Nichrome
60 per cent nickel, 24 per cent iron, 16 per cent chromium

52 Alloy
50 per cent nickel, 50 per cent iron

With the exception of Nichrome, all of these materials show quantities of gas components similar to those found in Monel and nickel-plated 304 stainless steel. Carbon monoxide was the predominant gas (6–30 l.μ/g), with smaller quantities of nitrogen (1–5 l.μ/g), carbon dioxide (1–3 l.μ/g), and hydrogen (1–2 l.μ/g). Nichrome V, with a higher chromium content, shows nitrogen as the predominant gas, and other gases in the same range as above.

TABLE VI

Gases obtained on heating tube materials to 1000°C

Material	Firing Treatment	Quantity of Gas, l.μ/g			
		H_2	N_2	CO	CO_2
Kovar	Line Hydrogen	1.8	5	30	1.3
70/30 Copper Nickel	Dry Hydrogen	1.4	1	10	1.8
Inconel	Dry Hydrogen	0.6	4	30	2.6
Nichrome V	Dry Hydrogen	1.0	17	6	1.2
52 Alloy	Dry Hydrogen	1.1	1	9	0.8

Discussion of results

Hydrogen.—When the metallic materials studied were heated to 1000°C after an initial 400°C exhaust bake out, the desorption of hydrogen was observed to be relatively small. Other observers have reported larger values ; Griessel[3], for example, found that 305 stainless steel desorbed about 30 l.μ of hydrogen per gram when heated to 1000°C. Most of this hydrogen, however, was evolved during a heating step at 300 to 600°C, and it is assumed that in the present work much of the hydrogen reported by Griessel was desorbed without measurement during the 1 hr exhaust at 400°C. Previous measurements indicated that the diffusion constant of hydrogen in nickel was 4×10^{-6} cm^2/sec at 400°C, and that depletion of hydrogen by diffusion from thin sections of nickel 0.005–0.010 in. in thickness should occur rapidly. The materials studied in this work evidently behave similarly on degassing, because permeation of hydrogen through all these materials was found to be rapid at temperatures below 400°C.

The permeation mechanism of hydrogen through these metallic materials is evidently a process similar to that described by Grimes[2] for hydrogen in nickel. In this case, hydrogen exists in solution in nickel, occupying interstitial sites. With one atmosphere of hydrogen on one side and a vacuum on the other, permeation of hydrogen through the material is a diffusion-limited process. On the one side, the nickel surface reacts with molecular hydrogen and atomic hydrogen is absorbed ; the concentration of atomic hydrogen reaches the solubility limit S. On the other side, hydrogen is desorbed from the surface as molecular hydrogen and is pumped away, and the concentration of atomic hydrogen in solution approaches zero. Thus, the permeation constant K is given by the relation

$$K = SD$$

where S is the solubility and D is the diffusion constant of hydrogen in nickel.

Nitrogen.—Like hydrogen, nitrogen is considered to exist in solution as atomic nitrogen in metals and alloys of the type investigated here. Permeation and degassing rates are presumably diffusion-limited. The solubility of nitrogen is increased by the presence of chromium or other metals which form nitrides ; thus, relatively large quantities of nitrogen are

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found to be desorbed when metals such as 304 stainless steel and Nichrome V are heated. In the present work, nitrogen was desorbed mainly at the highest temperature step (1000 °C). Degassing behavior thus indicates that the diffusion constant of nitrogen in these metals is small at the lower temperatures.

Permeation of nitrogen through the metallic materials was undetectable at a temperature of 850 °C. This result is not inconsistent with the degassing data, which show that appreciable degassing rates for nitrogen are not achieved much below 1000 °C.

Carbon monoxide and carbon dioxide.—Like hydrogen and nitrogen, the gases carbon monoxide and carbon dioxide are not considered to exist in solution in molecular form in the metallic materials investigated, but their component elements, carbon and oxygen, are individually soluble. Desorption of the molecular gases thus involves a surface reaction between dissolved carbon and oxygen. The diffusion of carbon is rapid compared to that of oxygen, so that the slow diffusion of oxygen would be expected to limit desorption rate. On the contrary, however, the degassing data show that the process is rather one of rapid depletion. Consequently, it is assumed that desorption rate is limited by diffusion of dissolved carbon to the surface and by its reaction with an excess amount of surface-bound oxygen.

The effects of hydrogen firing of Monel and stainless steel on desorption of CO and CO_2 may be examined in terms of this assumption. Table IV shows that desorption of CO and CO_2 from Monel is increased by a factor of three after the metal is fired in plant-line hydrogen. Dry-hydrogen firing, however, has the opposite effect, i.e. it reduces the observed quantities by a factor of three. It is concluded that an impurity element is oxidized at the surface by line hydrogen, and is reduced in dry hydrogen. This effect is not so clearly seen in the case of 304 stainless steel, which exhibits no change in the quantity of CO_2 desorbed when fired in dry hydrogen, but desorbs less CO.

The permeation of CO through these metal alloys involves a surface reaction at the incoming surface producing carbon and oxygen in solution ; the diffusion of both carbon and oxygen to the outgoing surface ; and a final reaction at the outgoing surface to produce the molecular gas. This process would clearly be no faster than the diffusion rate of oxygen. Consequently, the fact that a steady-state permeation rate of CO was undetectable at 850 °C is not inconsistent because the diffusion of oxygen is very slow at this temperature.

Summary

Hydrogen permeation through the metals Monel, 304 stainless steel, Kovar, Inconel, nickel, and 52 Alloy was found to be rapid even at temperatures approaching room temperature. These metals were not permeated by carbon monoxide, nitrogen, and helium at a temperature of 850 °C. No permeation of carbon dioxide through 304 stainless steel was observed at 750 °C. Similarly the ceramic materials alumina and forsterite were not permeated by hydrogen, nitrogen, carbon monoxide, carbon dioxide, helium, and air at 750 °C.

On the basis of type and quantity of gases evolved during a 1000 °C heating, materials may be divided into two groups. The first group includes Monel, nickel-plated steel, 304 stainless steel, Kovar, copper-nickel alloy, Inconel, and 52 Alloy. All these metals show similar quantities of gas components, with carbon monoxide as the predominant gas. The second group includes 304 stainless steel and Nichrome V, and shows nitrogen as the predominant gas.

Type 403 Monel and 304 stainless steel were examined for effects of gas firing prior to degassing. Both materials were improved (i.e. evolved less gas) when fired in dry hydrogen, and type 304 stainless steel was further improved by vacuum firing. However, Monel was unaffected by vacuum firing after dry hydrogen firing.

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Thermal Degassing of Tube Materials

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Introduction

Although the effective degassing of tube materials is one of the prime objectives of electron-tube processing and is the subject of many published works, little quantitative data is available on the gases obtained when the materials used in the construction of electron tubes are degassed. This paper describes the behavior typical of these materials when heated in vacuum.*

Measurement of thermal degassing of tube materials

Thermal evolution of gases from tube materials was induced by r.f. induction heating, in the case of metal samples, or by oven heating, in the case of both insulating materials and metals. Two temperature schedules were followed: under the first schedule, evolved gases were identified and measured as the sample was heated in four steps to 1000°C. This method provides a rapid test under conditions similar to the exhaust processing used for the elements of many tube structures. The second method provides for the determination of degassing rates during extended heating at a low temperature, after a short initial degassing treatment. This method permits a comparison of the degassing characteristics of tube materials under conditions resembling the operating conditions in finished electron tubes.

The metals were tested in the form of strip having a thickness of 0.005 in. Metal samples were washed first in ether, then in boiling deionized water, and were finally rinsed in ether and oven-dried. The ceramic materials, in the form of ¼ in. *dia.* rod, were washed in a detergent and then in water, rinsed in acetone, and oven-dried. Mica was tested in the form of sheet which was split to a thickness of 0.005 in., washed in ether, and oven dried.

The metal strip was mounted in the form of a cylinder on a small channel made of the same strip material for r.f.-induction heating. A thermocouple was spot-welded to the cylinder, and the sample was placed inside a glass bulb, exhausted, and baked with an oven at 400°C for 1 hr. Then the cylindrical sample was heated to higher temperatures, and gas evolution was measured. For oven heating, the strip or rod samples were cut to a length of 4 in. and sealed in a section of clear fused-silica tubing. Gas evolution during heating of the sample in a muffle furnace was then determined.

Gas batches were analyzed by the accumulation method[1], in which evolved gases are pumped away from the heated sample during a degassing period and are stored in the closed fore-volume system of the mercury collection pumps, as shown in Fig. 1. The accumulated sample is subsequently

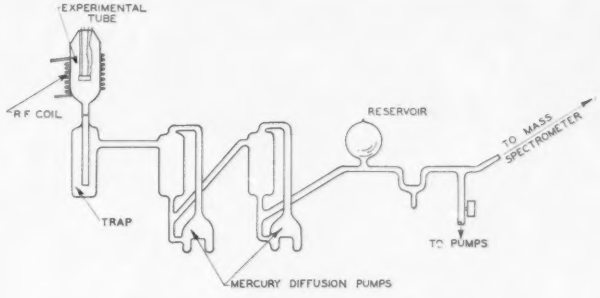

FIG. 1. Gas collection and analysis system.

leaked into the ion source of the mass spectrometer and spectrum is simultaneously scanned. The mass spectrometer used was the Model 21–620 supplied by the Consolidated Electrodynamics Corporation. The batch volume was 1 l., and the leak rate from the batch volume to the spectrometer source during scanning was 0.001 l./sec (for gas of molecular weight 28).

Experimental results

All the metallic materials exhibited a similar pattern of gas evolution when first heated. The persistent gases observed after a mild exhaust bake were hydrogen, nitrogen, carbon monoxide, and carbon dioxide. Measurements of these gases for the various materials studied are described below, and are summarized in Tables II and IV.

Nickel

An example of the degassing characteristics of nickel is shown in Table I, which lists the quantities of gases released when a sample of Type 330 nickel is heated to 1000°C. Carbon monoxide, the predominate gas, is evolved at a maximum rate at 850–1000°C. Carbon dioxide appears in relatively large quantities at the lower temperatures (550 and 700°C), but is not observed at the higher temperature. Nitrogen and hydrogen are evolved in small quantities at the higher temperatures. Figure 2 shows results of a low-temperature degassing test on this material. Gases were evolved and analyzed at a constant temperature of 400°C, after a short initial degassing of the sample at higher temperature. The material shows a substantial evolution of hydrogen, carbon monoxide, and carbon dioxide during the

*This work was supported by the U.S. Army Signal Corps under Contract No. DA-36-039-sc-78226 on "Electron Tube Materials, Gases and Getters".

TABLE I

Degassing of air-melted 330 nickel during heating to 1000°C

R.f. Heating Time, min	Temperature, °C	Quantity of Evolved Gas, l.μ/g		
		H_2	$CO + N_2$*	CO_2
20	550	0.1	2.6	2.5
20	700	0.2	5.3	3.2
20	850	0.2	9.1	0.9
20	1000	1.4	5.3	0.2
	Total	1.9	22.3	6.8

*Nitrogen not determined separately from carbon monoxide, but is less than 10 per cent of total.

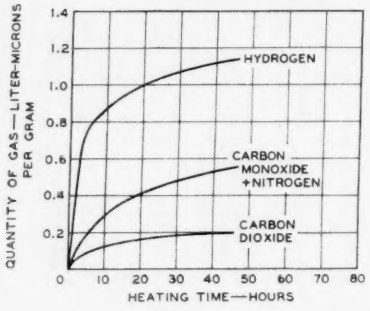

FIG. 2. Degassing of Type 330 nickel strip at 400°C.

first 20 hr of heating, with hydrogen as the predominant gas.

The total gas components observed for some representative commercial types of nickel heated step-wise to 1000°C are shown in Table II. These samples included a normal nickel (Type 330), an active nickel (DH 399), and a passive nickel (DH 499). Table II indicates that there is no relationship between the activity of a nickel and its gas content. Table II also shows that the use of vacuum-melted materials (Type 330, lot 3) does not assure a minimum gas content.

A high-purity nickel* which contained no single impurity in concentrations exceeding 0.005 per cent[2] was also studied. Table III lists the gases evolved from the nickel after samples were cleaned by different procedures. The first values, obtained from strip cleaned by degreasing only, are interesting in that the gas quantities are in the upper range of those reported for commercial nickels. The second values, showing smaller amounts of carbon monoxide, were obtained from strip which was surface-etched with a 1:1:1 solution of formic acid, hydrogen peroxide, and water, as outlined by Koontz[3]. A third set of values, obtained from strip which was both surface-etched and hydrogen fired, shows a possibly significant further decrease in the quantity of carbon dioxide.

TABLE II

Total gas obtained from tube materials heated to 1000°C

Material	Quantity of Evolved Gas, l.μ/g			
	H_2	$CO+N_2$	CO_2	O_2
330 Nickel, Lot 2	1.5	24	5.6	
330 Nickel, Lot 3	0.8	16	2.2	
330 Nickel, Lot 4	1.3	31	6.3	
330 Nickel, Lot 5	0.4	24	9.6	
DH 399 Nickel, Lot 1	0.6	12	2.9	
DH 499 Nickel, Lot 1	0.5	11	3.5	
CA-450 High-Purity Nickel	0.5	10	4.5	
Cold-Rolled Steel, Lot 1	1.4	250	5.1	
Aluminum-Clad Steel, Lot 1	18	16	4.2	
Nickel-Plated Steel, Lots 1, 2 and 3	1.9	26	4.6	
Carbonized Nickel-Coated Steel, Lot 1	78	450	25	0.05
Kovar, Lot 3	1.2	21	2.9	
Molybdenum, Lot 1	0.7	9	3.5	
Tungsten, Lot 1	1.0	6.7	2.8	
Titanium, Lot 1	520	1.0	1.5	
Tantalum, Lot 1	4.1	0.4	0.3	

TABLE III

Effect of surface treatment on degassing of CA-450 high-purity nickel

Pretreatment of Sample	Total Gas Evolved on 1000°C Heating, l.μ/g		
	H_2	$CO + N_2$	CO_2
Degreased Only	0.2	27.5	7.1
Surface-Etched	0.3	9.5	7.4
Surface-Etched and Hydrogen-Fired	0.6	10.4	4.5
Values from Morrison[4] for CA-450 Nickel	18	4.5	1.3
	7	8.1	2.8

*Nitrogen not determined separately from carbon monoxide, but is less than 10 per cent of total.

Cold-rolled steel and coated steel

For improved properties in electron-tube applications, low-carbon steel is often plated with nickel, clad with aluminum, carbonized on a nickel coating, or provided with other similar coatings. Table II lists the gases evolved when both coated and uncoated samples were r.f.-heated to 1000°C. Uncoated steel shows quantities of carbon monoxide and nitrogen which are about ten times larger than those observed for nickel. Nickel-plated steel and aluminum-clad steel show these gases in lower quantities. Hydrogen appears in substantially larger amounts in the aluminum-clad steel. Gas-carbonized, nickel-coated steel shows substantially larger quantities of all gases, including a small amount of oxygen.

Table IV shows the results of low-temperature degassing of steel and coated-steel strip heated at 400°C for 40 hr. Although the individual gas components vary among these different materials, the range of variation is not as great as might be expected from examination of the degassing results obtained at higher temperatures shown in Table II.

*Supplied by Mr. J. O. McNally of the Bell Telephone Laboratories.

TABLE IV

Degassing of materials by continued heating at 400°C for 40hr.

Material	Initial Outgassing Temperature, °C	Treatment Time, min	Total Quantity of Evolved Gas, l.μ/g			
			H_2	$CO+N_2$	CO_2	O_2
330 Nickel	800	10	1.1	0.5	0.2	
Cold-Rolled Steel	800	10	0.2	0.8	0.014	
Aluminum-Clad Steel	800	10	1.6	0.05	0.3	
Gas-Carbonized Nickel-Coated Steel	800	10	1.1	0.1	0.03	
Tantalum	800	10	0.7	0.004	0.002	
Copper	400	60	0.06	0.12	1.3	
Mica	400	60	1.5	0.2	0.3	0.01–0.5
Steatite, Forsterite, Alumina	800	10	0.01	0.001	0.002	0.0002

Other metals

The higher-temperature degassing results observed for the metals Kovar*, molybdenum, tungsten, titanium, and tantalum are also summarized in Table II. Of these metals, Kovar, molybdenum, and tungsten show gases similar in quantity to those observed for nickel. Titanium shows exceptionally large quantities of hydrogen, with other gases at lower levels. Tantalum shows moderate quantities of hydrogen, with nitrogen, carbon monoxide, and carbon dioxide at low levels; during lower-temperature degassing, evolution of the latter gases from tantalum is exceptionally low. Table IV shows exceptionally large quantities of carbon dioxide for copper, which was degassed only during low-temperature heating at 400°C.

Ceramic materials

The gases evolved from clear ruby mica (muscovite) during extended heating at 400°C are summarized in Table IV. This material shows moderate quantities of hydrogen, carbon monoxide, and carbon dioxide, whereas oxygen appears in variable quantities. In addition to the gases determined quantitatively, a considerable evolution of water vapor was observed. Also an unidentified gas giving small peaks at $M/e = 19$ was seen.

Steatite, forsterite and alumina ceramic materials were studied for gas content by use of the low-temperature method, in which the sample is first degassed at 800°C for 10 min, and evolved gases are then analyzed during extended heating at 400°C. Significant quantities of gases were found when this degassing schedule was applied to various metals and to mica. When the low-temperature schedule was applied to the ceramic materials, however, no gas components were observed. Gas evolution is thus estimated to be less than the background levels shown in Table IV for these materials.

Discussion of outgassing data

Hydrogen desorption by metals

The ferrous metals are readily permeated by hydrogen at moderate temperatures; the permeation rate is diffusion-limited for hydrogen pressures of about 1 atm. Desorption should similarly be diffusion-limited, and because diffusion is rapid, the complete desorption of hydrogen from these metals should be readily achieved with moderate heating.

The diffusion-limited desorption of a dissolved gas from a thin plate is given by the relation[4]

$$f = 1 - \frac{8}{\pi^2}(e^{-z} + e^{-9z}/9 + e^{-25z}/25 + \ldots)$$

where: f is the fraction of total gas content which has diffused to the two surfaces at time t,

$z = \pi^2 Dt/4a^2$,

$2a$ is the thickness of the sheet of metal in cm,

t is time in sec,

D is the diffusion constant of the gas in the metal in cm^2/sec.

The series converges rapidly and for values of z greater than 0.2 only the first term in parentheses is retained. Thus the equation may be rewritten as follows:

$$(1-f) = 8e^{-z}/\pi^2$$

or $\log (1-f) = \text{constant} - 1.07\, Dt/a^2$

The last relation can be used to calculate D from gas-evolution data taken at constant temperature. The quantity $\log (Q_0-Q)$ is plotted as a function of time, where Q is the observed amount of evolved gas, and Q_0 is a constant chosen to yield a straight-line plot. This value of Q_0 physically represents the total initial gas quantity present in the metal. From the slope $-S$ of this plot, the constant D is calculated by the relation $D = a^2S/1.07$.

Figure 2 shows data of hydrogen evolution from nickel heated at 400°C over a 45 hr period. If plotted as outlined previously, the quantities of hydrogen can be represented by a straight line having the constants $D = 2.3 \times 10^{-10}$ cm^2/sec. and $Q = 1.2$ l.μ/g. The assumption that diffusion limits degassing rate can be tested by comparison of the calculated value of D with directly measured values of D. The diffusion of hydrogen in nickel has recently been reviewed by Grimes[5], who gives the following relation for the diffusion constant for the temperature range from 450 to 850°C:

$$D = 0.0095 \exp(-10{,}300/RT) \text{ cm}^2/\text{sec}.$$

At 400°C, a value of D of 4×10^{-6} cm^2/sec. is obtained from this relation. This value disagrees substantially with that obtained for the present tests and indicates that desorption of hydrogen should be complete after only a few minutes heating time at 400°C. The delayed desorption observed during 45 hr of heating time may be due to the existence of hydrogen in inclusions or voids in the nickel.

Similar data on the desorption of hydrogen from cold-rolled steel at 400°C shows a depletion curve lasting many hours, from which an unreasonably high diffusion constant would be derived. A similar situation is revealed in the data on carbonized nickel-coated steel. Hydrogen desorbed by aluminum-clad steel shows a different pattern, however, probably because the aluminum cladding acts as a limiting barrier. As indicated in Table II, this material shows substantial hydrogen evolution when heated to 1000°C. Thus, hydrogen in aluminum-clad steel (both sides clad) is more tightly held than in cold-rolled steel.

*Carborundum Company, Blainsville, Pa.

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Desorption of CO and CO_2 by metals

The desorption of carbon monoxide from nickel at temperatures of approximately 1000°C was found by Smithells and Ransley[6] to be diffusion-limited; the diffusion rate corresponds to the diffusion constant of carbon in nickel analyzed at the same temperatures. The authors concluded that carbon monoxide could not be present in nickel as a dissolved gas, and that the desorption of carbon monoxide from nickel was derived from a reaction between dissolved oxygen and carbon.

The data obtained from the desorption of carbon monoxide from nickel at 400°C (Fig. 2) can be examined in terms of diffusion of dissolved carbon as the limiting rate. The diffusion constant is obtained by extrapolation of higher-temperature data, and is assumed to have a value of 10^{-13} cm^2/sec. It is readily shown that in a period of 40 hr only a thin surface layer of nickel approximately 2μ deep could contribute carbon by diffusion to a surface reaction producing CO or CO_2. For this case, therefore, the nickel strip of 0.005 in. (125μ) thickness can be treated as a semi-infinite body, and the rate of carbon reaching the surface by diffusion is given by

$$Q = 2C_0\sqrt{(Dt/\pi)}$$

where Q is the total amount of carbon which has diffused to the surface in time t, and C_0 is the initial (uniform) concentration of carbon in the nickel. The concentration of carbon in this lot of nickel is 0.055 wt per cent, or approximately 7000 $l.\mu/cm^3$. When this value of C_0 is used with the assumed value of D, Q expressed per gram sample of 0.005 in. thick strip has a value of

$$Q = 2.6\sqrt{t}\ l.\mu/g\ hr$$

where t is the time in hours. If the data of Fig. 2 are plotted as a function of square root of time, the quantities of CO and CO_2 can be represented as straight lines defined as follows:

Carbon monoxide	$Q = 0.084\sqrt{t}$
Carbon dioxide	$Q = 0.032\sqrt{t}$
Total carbon	$Q = 0.116\sqrt{t}$

The calculation based on carbon diffusion thus shows reasonably good agreement with the data of Fig. 2 in view of the uncertainty of both the initial concentration of carbon in the surface layers (an average concentration was assumed) and the value of the diffusion constant of carbon in nickel at this temperature.

In this case, oxygen must be available at the nickel surface to react with carbon diffusing out to produce the gases CO and CO_2. The degassing data for nickel obtained during the present work usually indicate a ratio of approximately 3 parts CO to 1 part CO_2 at the lower degassing temperatures of 400–700°C. During a degassing test, the evolved gases are in equilibrium with the hot nickel surface; the observed ratio of CO/CO_2 thus itself indicates that at these temperatures there is an excess of oxygen in the system, which is probably in the form of a surface film of nickel oxide. The lower-temperature desorption of CO and CO_2 from nickel, therefore, appears to be defined by an excess of oxygen residing at the surface, which reacts with carbon diffusing out from a thin surface layer.

Tantalum is another refractory metal which would normally be degassed at high temperatures. This metal, however, is interesting in that it desorbs exceptionally low quantities of CO and CO_2 on first heating. Low quantities of CO and CO_2 are also desorbed when tantalum is degassed for extended periods at 400°C after a short degassing treatment of 800°C.

Outgassing of ceramic materials

The ceramic materials forsterite, alumina and steatite show no detectable low-temperature evolution of gas at 400°C after a short degassing treatment at 800°C. Steatite, however, desorbed quantities of hydrogen, carbon monoxide, carbon dioxide, and oxygen when heated to temperatures between 800 and 1000°C. The mechanism of desorption of these gases, some of which may exist in solution in the glassy phase of the materials, is not known.

Mica

Because mica exfoliates at high temperatures, the preliminary 10 min, 800°C degassing schedule is not used. On extended heating at 400°C, however, mica shows a substantial desorption of hydrogen, carbon monoxide, nitrogen, carbon dioxide, and oxygen. The variable amounts of oxygen found suggest that a part of the desorbed gases may be trapped or occluded in fissures formed by cleavage planes of the strip material.

Conclusions

The following general remarks summarize and interpret the desorption characteristics of the materials studied:

Nickel

The composition of commercial nickels and the procedures used for melting (vacuum versus air-melting) were not found to affect degassing behavior. The fact that nickel-plated iron resembles nickel more than iron in degassing behavior indicates the importance of the surface in determining evolution of gas. The data further suggest that gas evolution in commercial nickels deoxidized with active metals may be secondarily related to carbon content, and the severity of inclusions present. The best of the commercial materials were low in carbon and nearly free of inclusions.

Hydrogen, carbon monoxide, carbon dioxide, and nitrogen were evolved by nickel during low-temperature heating after an exhaust bake-out. Analysis shows that most of the hydrogen is removed early and at low temperatures because of its rapid diffusion rate in nickel. Residual amounts are believed to represent the effects of hydrogen locally bound in inclusions in the nickel. Nitrogen is usually found as a small percentage of carbon monoxide and was not particularly studied in the present work.

The carbonaceous gases, CO and CO_2, are the most important because of their effect on the gaseous environment in electron tubes. Desorption of these gases is explained by a surface reaction of carbon and oxygen. The desorption rate appears to be limited by the rate of diffusion of dissolved carbon to the surface; at 400°C, a desorption rate calculated from the average carbon concentration in nickel and carbon-diffusion constant shows fair agreement with observed values. This mechanism of desorption requires an excess amount of surface-bound oxygen. The existence of this excess oxygen

is demonstrated by the simultaneous evolution of CO and CO_2 at the lower outgassing temperatures of from 400 to 700°C.

Iron

Iron generally shows a greater desorption of gases than nickel because of its higher gas content and higher diffusion rates. Various coatings used on iron strip modify its degassing characteristics. Aluminum-clad strip, for example, shows a persistent evolution of hydrogen, which is believed to be caused by hydrogen's slow diffusion rate in aluminum. Hydrogen degassing for aluminum-clad strip, as a result, is difficult.

A nickel coating substantially reduces the desorption rate for CO and CO_2 to values characteristic of nickel. This observation is understandable on the basis of the assumptions made previously for desorption of these gases from nickel; namely, that oxygen for CO and CO_2 desorption comes from the surface, whereas carbon is supplied by diffusion from the body of the strip. The degassing properties of nickel-coated, gas-carbonized strip are dominated by the carbonized layer, which degasses strongly when heated to the higher temperatures, but thereafter shows a low level of desorption of CO and CO_2 at lower temperatures.

Molybdenum, tungsten, titanium, and Kovar

CO and CO_2 desorption by these metals when first heated to 1000°C follows a pattern similar to that found for nickel. The mechanism of desorption is possibly similar.

Tantalum

The degassing properties of tantalum are interesting in that exceptionally small quantities of CO and CO_2 were found both at high and low temperatures.

Copper

One lot of copper strip studied showed exceptionally low evolution of hydrogen and high evolution of carbon dioxide. However, because this material is sensitive to cleaning and prior processing, the gases observed could be radically altered by changes in processing.

Ceramic materials

Dense samples of steatite, alumina, and forsterite showed substantially no evolution of gas when heated for extended periods at 400°C after a short outgassing treatment at 800°C. For moderate temperatures, these materials thus are more satisfactory than commercial glasses, which show a substantial desorption of water when heated at 400°C.

Mica was found to desorb large quantities of hydrogen, carbon monoxide, nitrogen, carbon dioxide, and oxygen on extended heating at 400°C. Without the use of a high-temperature degassing treatment, this material would appear to be fairly unsatisfactory for use at those moderate temperatures.

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ADVANCES IN ELECTRON TUBE TECHNIQUES

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A Comparison between the Evaporation Characteristics of a Crucible and a Ring Source*

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The properties of evaporated films largely depend on the uniformity of the evaporation parameters achieved during their deposition. Several types of evaporation sources have been investigated. In this paper, data on the crucible and the ring source as sources for evaporated films are presented and their advantages and disadvantages are discussed. For both techniques, the experimental setup, the distribution of film thickness, and the variations of chemical composition over the area of a substrate are described in detail. The experimental results are compared with theoretical considerations.

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Introduction

The evaporation of alloys has always been a difficult problem. Usually, the vapor pressures of the components (e.g. nickel and iron) are not the same. Therefore, the chemical composition of the evaporated film differs from that of the source[1]. Furthermore, this difference frequently depends on the evaporation temperature. If a certain chemical composition of the evaporated film is desired, not only must the composition of the melt be carefully chosen, but the evaporation temperature must be kept constant.

In the practical application of evaporated films, it is necessary that the film be uniform in chemical composition and thickness over a large substrate area. The realization of these demands is possible only if the right type of evaporation source is chosen. It is the purpose of this paper to give the experimental results of two types of sources which have been investigated.

Advantages and disadvantages of a crucible and a ring source

Several factors should be considered in selecting an evaporation source. The ideal source would be a " free source ", i.e. one in which the evaporant is not in contact with any other material. This guarantees an evaporated film free of contamination due to the source container. The source should yield films of uniform thickness over the desired substrate area. Furthermore, the distance between source and substrate should be minimized in order to obtain high deposition rates. Further, the temperature of the source must be uniform over the entire evaporation area to ensure uniformity in both evaporation rate and chemical composition.

The following text deals with the sources investigated and considers the degree of perfection one would expect to obtain in the light of the above requirements.

The crucible. It is a common technique to place the metal to be evaporated in a ceramic crucible[2]. This procedure has the disadvantage that contamination of the melt by the crucible material is likely. Indeed, it was observed that, in each evaporation using a crucible, slag is formed on the surface of the melt. Part of this slag is probably made up of metal oxides, but a large portion of it certainly consists of crucible material. The total amount of slag varies from one melt to another. It depends on the crucible material and often on the number of times the crucible has been used for evaporations. Especially in the case of silica crucibles, it was found that both the melt and the evaporated film contained silica.

The slag present at the surface of the melt influences the evaporation rate. To obtain uniform rates from run to run, the source temperature must be altered according to the amount of slag present. Since the chemical composition is directly dependent upon the source temperature, this is achieved at the expense of uniformity in chemical composition.

Finally, the evaporation characteristics of a crucible are unfavorable with respect to thickness distribution. The thickness of the evaporated film is at a maximum above the center of the crucible and decreases radially[3]. To maintain

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the film thickness uniform within 2 per cent, it is necessary that the source to substrate distance be five times as great as the diagonal of the substrate. This problem becomes increasingly important when it is intended to evaporate on a fairly large substrate area, since the deposition rate is inversely proportional to the square of the distance between source and substrate.

Ring source. From theoretical considerations one would conclude that the highest uniformity in thickness over a large substrate area could be obtained by evaporating from a ring-shaped source, with only a relatively short distance between source and substrate necessary. The simplest form of a ring source consists of a wire of the required chemical composition, bent into a ring and resistance-heated. The possibility of contamination of the source material by the source container is avoided completely. Provided the diameter of the wire is the same throughout its length, the temperature during evaporation and, therefore, the rate of deposition and the chemical composition of the deposit are uniform. The main disadvantage of such a source is that the evaporation takes place from the solid state, where the vapor pressures of both nickel and iron, used in these evaporated films, are fairly low[4]. The slow rate of evaporation is partially compensated for by the short distance between the source and the substrate.

Let us now compare the actual evaporation characteristics of the sources with the above considerations.

The crucible

Experimental setup. Fig. 1 is a photograph of the interior of the bell jar. The crucible, which can be seen in the lower part of the figure, is supported by a water-cooled r.f. coil (used for induction heating). In order to prevent an excessive temperature gradient, two crucibles are used, one inside the other. The inner one contains the melt, while the outer one is in contact with the cold r.f. coil.

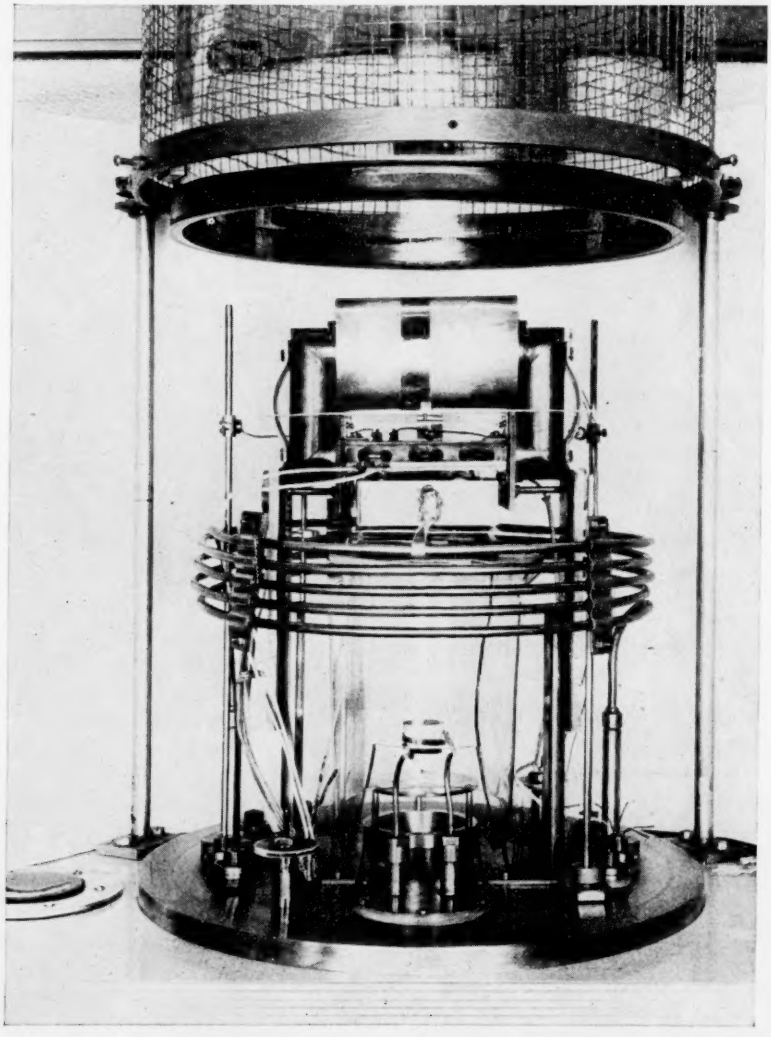

FIG. 1. Interior of bell jar with crucible assembly.

In the upper part of the figure, the substrate holder (containing the substrates and the mask) and the substrate heater can be seen. This assembly is attached to an electromagnet, the pole pieces of which are extended by mild steel plates to yield a uniform field over the substrate area. A long Meissner-type cold trap (copper tubing through which liquid nitrogen is circulated)[5] enables us to obtain fairly low pressures (usually 2×10^{-6} mm Hg) before the evaporation is started.

The substrate (Fig. 2) contains four glass slides of $0.039 \times 1 \times 3$ in. One slide (the monitor) is used to measure the film thickness by conductivity during evaporation. Part of this slide is used afterwards for analysis of the chemical composition. Four bits of 1 cm diameter are evaporated on each of the other three slides. The bits are numbered as shown in Fig. 2.

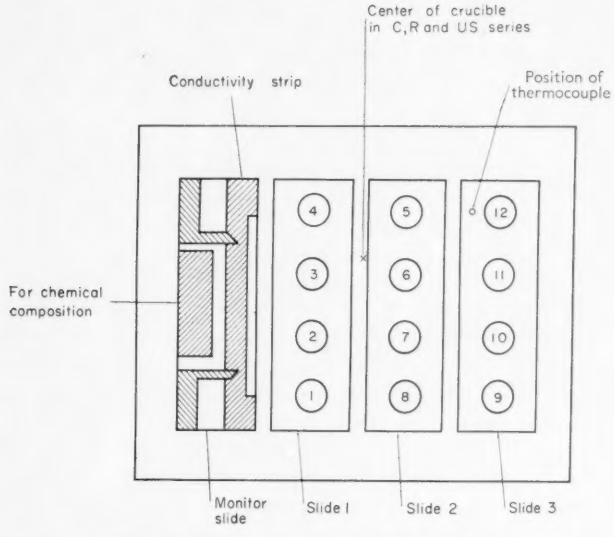

FIG. 2. Substrate for crucible technique.

Film thickness. For the measurement of the thickness of the ferromagnetic films, three methods are used : multiple-beam interferometry, X-ray fluorescence, and film output voltages (E_0) obtained from the B-H loop tester.

The accuracy of these three methods can be determined from the following considerations. Multiple-beam interferometry is claimed to give results with an ultimate error of approximately 3 Ångström units (Å)[6]. This very low value can be obtained only when extreme care is taken. Under normal laboratory conditions, errors between 30 and 50 Å are usually obtained. When the edge of the film is distorted or is not steep enough, the error is even higher (5 per cent for a 2000 Å film).

X-ray fluorescence has been used to determine the chemical composition and the thickness of evaporated films. In the case of nickel–iron films, the error in analyzing the chemical composition is approximately ± 1 per cent of the component which is present in the smaller amount (iron) while the error in precision of measurement is approximately ± 0.3 to ± 0.4 per cent. From such a chemical analysis, the amount of material per unit area (given in $\mu g/cm^2$) can be calculated. Since both the X-ray counts for nickel and iron enter into the calculation, the error is approximately ± 2 per cent, and the precision error is approximately ± 0.6 to ± 0.8 per cent. The relative thickness is determined from the mass per unit area, assuming bulk density equals film density. Accuracy and precision are the same as for the calculation of the mass.

With regard to the use of the output voltage of the B-H loop tester as a measure of film thickness, it can be stated that E_0 is proportional to the change in total flux. So long as the flux density and the geometry of the bits do not change, E_0 is proportional to the thickness also. This assumption was checked and found to hold, at least for the film samples which were made simultaneously, and for runs with the same chemical composition, where the flux density is approximately the same. For measurements of the thickness over the area of the substrate, E_0 was used most extensively, since it is easier to obtain than either optical or X-ray fluorescence measurements. The output voltage (E_0) is read from an oscilloscope. This can be done with an error of approximately ± 3 per cent.

For the investigation of the thickness distribution, several series of runs were made. In each series, the conditions of evaporation were kept as constant as possible. Then, the output voltages for each bit position were added and averaged. These average values are plotted in Fig. 3 vs. the bit position

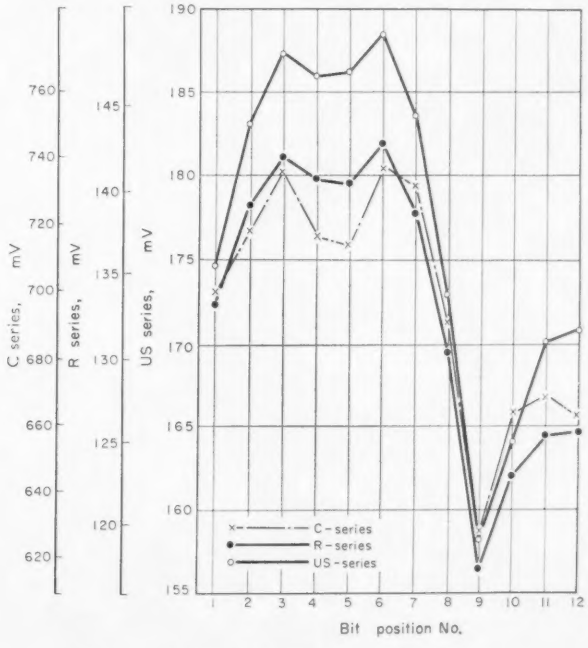

FIG. 3. Thickness distribution over substrate area.

for three series of runs. It is seen that the characteristics of all three curves are the same, although the output voltages differ by a factor of 5. This shape of the curves is evidently caused by the experimental conditions.

To compare the results of the different methods for thickness measurement with each other, the curves for the output voltage and the thickness (obtained by X-ray fluorescence) for the same run were plotted and are shown

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in Fig. 4. It can be seen from these curves that the agreement of these methods is excellent. The difference between them is usually less than ± 1.5 per cent, although the scales are not exactly fitted together. At the same time, this fact indicates that the assumptions on the proportionality between E_0 and film thickness are valid.

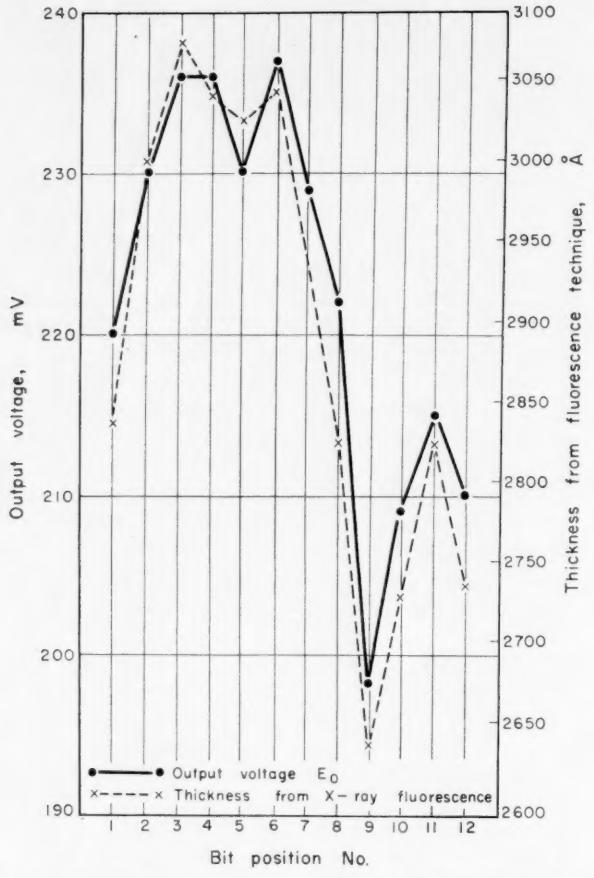

FIG. 4. Comparison between thickness distributions obtained by output voltage and X-ray fluorescence measurements.

The shape of the curves in Fig. 4 resembles that of those in Fig. 3 very closely. Since the X-ray fluorescence technique gives the most accurate measurement of relative thickness, the former curve has been used to compare the theoretical and the actual thickness distribution over the substrate area.

It was intended to analyze theoretically which thickness distribution is to be expected from a crucible. The melt in a crucible is a " surface source ", but since the surface of the melt has a diameter of 23 mm, it was uncertain if this large evaporating area would fulfil the requirements of the " small surface source " (cf. Ref. 3, p. 145). Therefore, the melt was considered to consist of a number of concentric " rings of small surface sources " (cf. Ref. 3, p. 153). The diameter of the largest ring was assumed to coincide with the diameter of the surface of the melt. Since for this ring (and for the actual distance between melt and substrate of 240 mm) the thickness distribution was exactly the same as for a small surface source with the equal distance between melt and substrate, it was assumed that the equations for the small surface source give a good representation of the deposition characteristic for the geometry of the experimental setup.

The thickness distribution is usually given as a plot of the thickness vs. the distance between the point under consideration and point A (above the center of the crucible in the plane of the substrate). Since the location of point A is difficult to measure with the required accuracy, it was determined from the experimental data. In Fig. 5, the centers of the bits are marked. Then, concentric circles—each describing a plateau of equal thickness—were drawn through the marks in such a manner that the thickness decreased radially. The center of the circles was assumed to be point A.

In Fig. 6, the thickness is plotted vs. the distance between

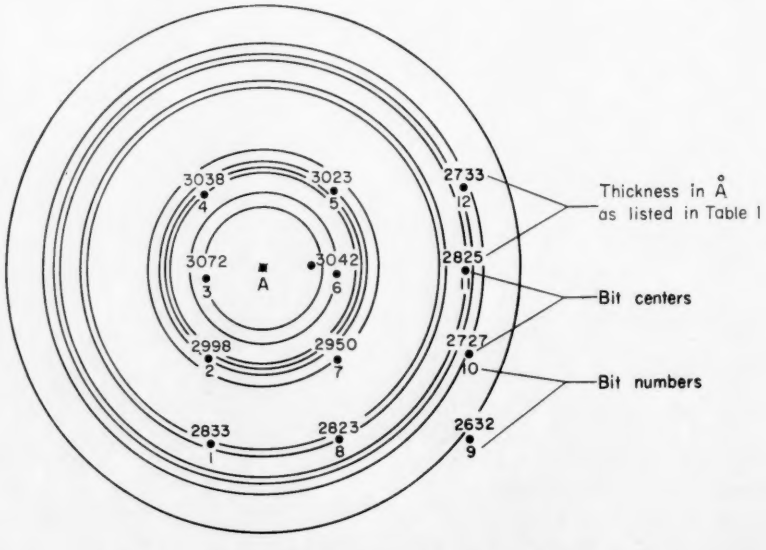

FIG. 5. Determination of point A above center of crucible.

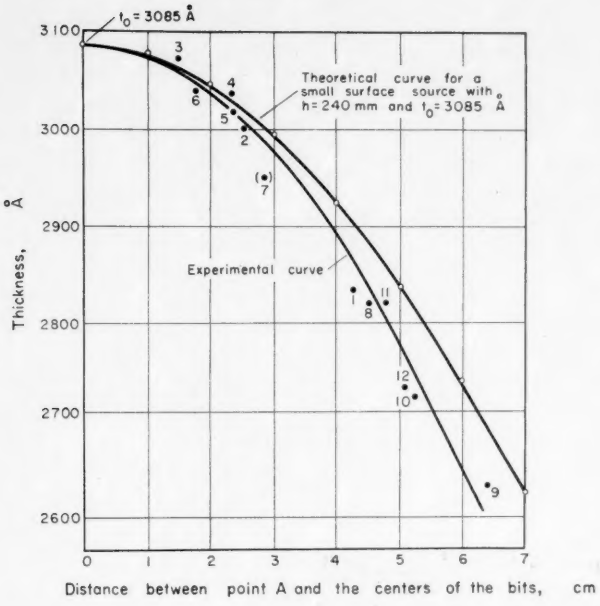

FIG. 6. Theoretical and experimental thickness variation.

point A and the actual centers of the bits. The deviation of the points from the curve is usually less than ±1 per cent and is therefore well within the accuracy of the detection method, especially if the inaccuracy in the determination of point A is taken into account.

In the same figure, the theoretical curve has been plotted for a "small surface source" with $h = 240$ mm and $t_0 = 3085$ Å (t_0 is the thickness at point A and is obtained by extrapolating the experimental curve to zero distance on the abscissa). It is seen that the experimental and the theoretical curve coincide for smaller distances (up to about twice the radius of the crucible) and that the difference between them becomes gradually larger with increasing distance. This can be explained by the fact that the masks over the substrates might have some shadowing effect for larger angles of incidence of the vapor stream.

The thickness distribution given by the crucible, however, does not always have the pattern shown in Figs. 3 and 4. It sometimes happens that the inner crucible which contains the melt is tilted, although the outer one is in the usual position. Such tilting can change the thickness distribution completely. In order to obtain the same distribution from run to run, special care must be taken to make sure that the evaporation crucible is maintained precisely in the same position.

Distribution of chemical composition. In all evaporation processes, a part of the monitor slide is taken for chemical analysis. For this purpose, colorimetric techniques are used,

TABLE I

Distribution of Chemical Composition and Thickness for a Crucible Evaporation

	Composition		Thickness		
			X-Ray fluorescence		Loop test
Bit No.	% Fe	% Ni	(μg/cm^2)	(Å)	E_0 (mV)
1	19.4	80.6	246.2	2833	220
2	19.4	80.6	260.5	2998	230
3	19.3	80.7	267.0	3072	236
4	19.3	80.7	264.0	3038	236
5	19.1	80.9	262.7	3023	230
6	19.4	80.6	264.3	3041	237
7					229
8	18.8	81.2	245.3	2823	222
9	19.2	80.8	228.7	2632	198
10	18.9	81.1	237.0	2727	209
11	19.3	80.7	245.5	2825	215
12	19.0	81.0	237.5	2733	210
Average	19.19 (%)	80.81 (%)	250.8 (μg/cm^2)	2886 (Å)	223 (mV)
Standard deviation	± 0.2 (%)	± 0.2 (%)	± 12.8 (μg/cm^2)	± 147 (Å)	± 12 (mV)
Percentage deviation			± 5.1 (%)	± 5.1 (%)	± 5.4 (%)

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which yield an error of ± 1 per cent or less, depending on the amount of material available. This technique cannot be used, however, to investigate the distribution of the chemical composition over the area of the substrate. The amount of material in a bit of 2000 Å thickness is too small for an accurate chemical analysis by this method. For tests of chemical distribution, only the X-ray fluorescence technique is used. This method is suitable for the investigation of thin-film thickness. Since we are interested in the differences in composition of adjacent bits, only relative measurements are required. For this purpose, the high precision of the X-ray technique is especially advantageous.

The results of an X-ray investigation are reproduced in Table I. The percentage values of iron and nickel are listed in the first two columns. The third and fourth columns are labelled, respectively, mass per unit area and thickness in Ångström units. Information concerning the output voltage of the bits is also included in the table (the thicknesses and output voltages are those plotted in Fig. 4). It is seen from the results in Table I that the variation in chemical composition is very small. The standard deviation, calculated by using the method of least squares, is only ± 0.2 per cent and is therefore well within the precision of the X-ray technique. The distribution of the chemical composition seems to be completely random.

It might be added that Table I gives the results for a typical run. Even in cases where the magnetic properties of the bits were abnormal, neither the variation of thickness nor that of the chemical composition was remarkably larger than the figures reproduced in the table.

Ring source

Interior of bell jar. Fig. 7 is a photograph of the evaporator. The Helmholtz coils are located on both sides

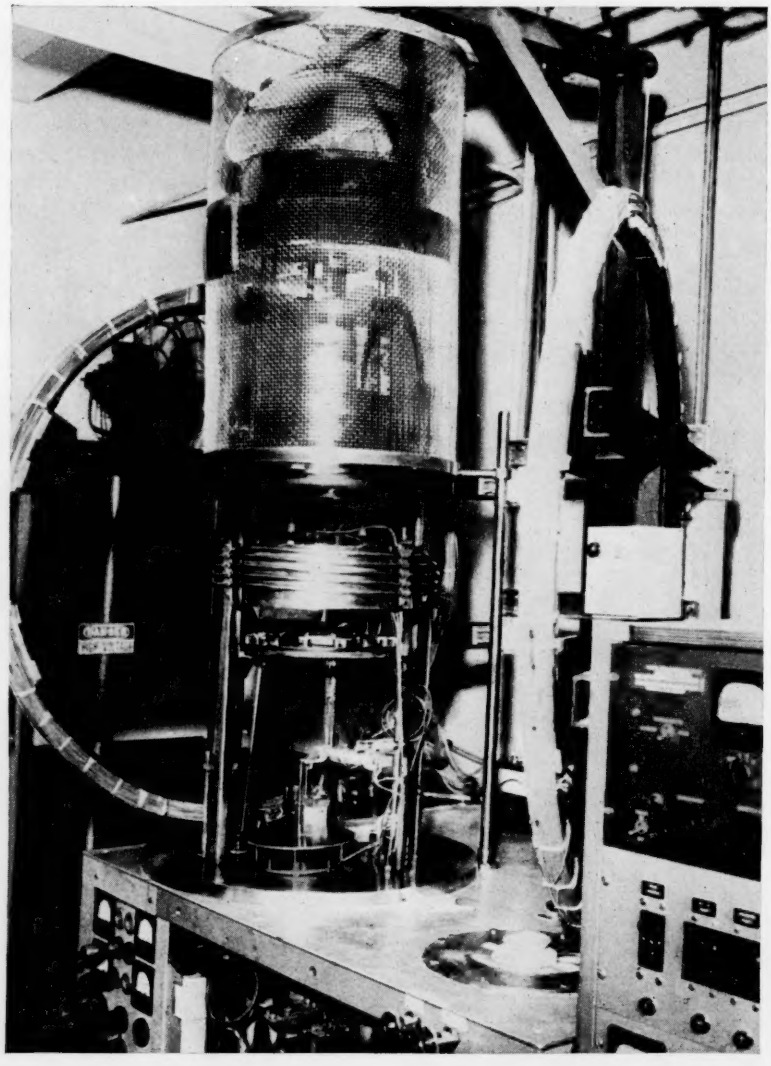

FIG. 7. Evaporator with ring source.

of the bell jar. For a current of 20 A, a uniform field of 80 oersted can be obtained, which is sufficient to yield a preferred direction of magnetization in the ferromagnetic films. A densitometer assembly which is located above the base plate serves to detect film thickness and rate of evaporation. The ring source is visible in the center of the figure, while the substrate holder above it is covered by the Meissner trap. The schematic sketch of the bell jar in Fig. 8 gives a better picture of the details. In the upper part, the substrate heater can be recognized, and the substrates and the mask are indicated. The ring source itself consists of 0.050 in. diameter Ni–Fe wire, which is wound into two rings. These rings are supported by ceramic rods which are fastened to a stainless steel frame. The frame is water-cooled in order to avoid outgassing when the ring source is heated.

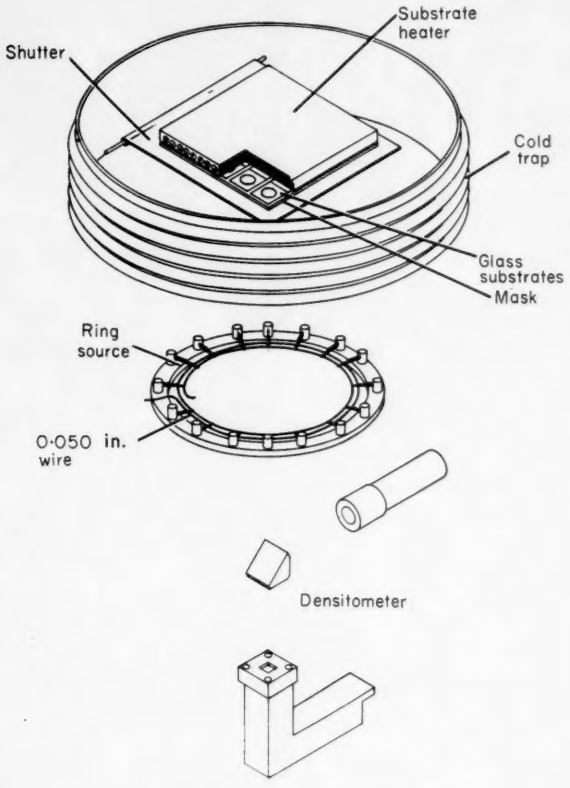

FIG. 8. Isometric view of ring source.

The dimensions of the ring source were derived from the following considerations. It was intended that the thickness variation of the evaporated film be less than 1 per cent over a given substrate area (9×13 cm). Using Holland's formulas (cf. Ref. 3, p. 153), it was felt that the goal might be achieved with a source radius of $R = 1$ and a distance from source to substrate of $h = 1.1$ when the outermost point of the substrate area has a distance from the substrate center (above the center of the ring) of $A = 0.7$. Since A was known to be 8 cm, 11.5 cm was chosen for R (mean diameter of the two rings) and 12.6 cm for h.

Composition of the evaporated film. As mentioned in the introduction, the chemical composition of the evaporated film is different from that of the melt and is a function of the evaporation temperature. Usually, the film contains more iron than the melt (cf. Ref. 1), leaving the melt, therefore, rich in nickel. In the case of the crucible source, this shift of melt composition is usually negligible, since the amount of material evaporated is small compared with the total mass of the melt. But in the case of the ring source, a much higher percentage of the material is evaporated per unit time. The result is that the composition of the film is very likely to change as the evaporation time progresses. In order to investigate this question, the following experiment was performed.

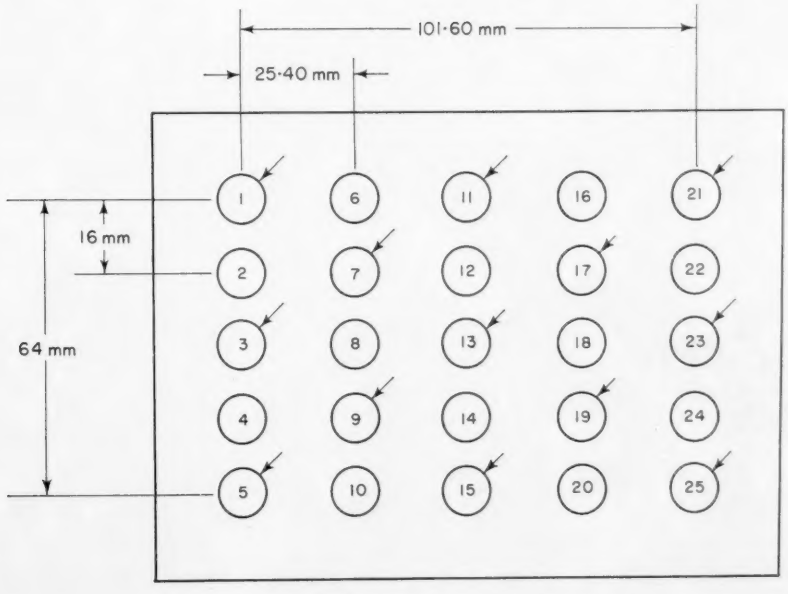

FIG. 9. Substrate for ring source evaporation.

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Three pieces of 2 in. diameter glass tubing were mounted in a bell jar. A straight piece of the alloy wire normally used for the ring source was run through the center of this tubing. After the wire had been heated at a constant current for 10 min, the bell jar was opened and the film deposited on the inside of the tubing was analyzed chemically. This procedure was repeated with the same wire several times.

TABLE II

Percentage of Iron Evaporated as a Function of Evaporation Current and Time

Current (A)	Evaporation time (min)			
	0–10	10–20	20–30	30–40
19	21.4			
20	21.4			
21	23.7	22.2	22.4	
22	20.3	20.1	18.5	18.4
23	19.5	18.4	17.6	
24	18.5			

Each evaporation lasted for 10 min and was performed with the same current. The results of these experiments are shown in Table II, where the percentage of iron as detected by chemical analysis is listed. While the composition of the alloy wire is 17 per cent Fe and 83 per cent Ni, this composition was only approached in the evaporated film. It was found that the longer the evaporation time or the higher the evaporation temperature (or current), the closer were the compositions of wire and film. It was impossible to evaporate at 24 A for much longer than 10 min or at 23 A for more than 30 min. It seemed that the wire burned out as soon as the compositions of wire and film were approximately equal. On the other hand, the lower the evaporation temperature, the more iron-rich was the deposited film. Naturally, the wire would in time have become more and more nickel-rich. This effect can be observed as a decrease of iron evaporation with increasing evaporation time.

These experiments were performed under fairly crude conditions. Their purpose was to give a first orientation on the problems encountered in the evaporation of alloys. More refined experiments are underway, and their results will be reported later.

Distribution of thickness and chemical composition. It was intended to investigate whether as uniform a distribution

TABLE III

Distribution of Chemical Composition and Thickness for a Ring-source Evaporation

	Composition		Thickness			
Bit No.	% Fe	% Ni	X-Ray fluorescence (μg/cm^2)	(Å)		Loop test E_0 (mV)
1	20.6	79.4	132.1	1520	5	95
3	20.4	79.6	131.9	1518	7	95
5	20.6	79.4	131.2	1510	15	100
7	20.7	79.3	133.8	1540	15	95
9	20.5	79.5	132.5	1525	0	95
11	20.4	79.6	131.6	1515	10	100
13	20.2	79.8	133.8	1540	15	100
15	20.4	79.6	132.3	1523	2	95
17	20.3	79.7	132.3	1523	2	95
19	20.5	79.5	132.3	1523	2	95
21	20.4	79.6	132.7	1527	2	95
23	20.5	79.5	133.8	1540	15	95
25	20.5	79.5	132.7	1527	2	95
Average	20.5%	79.5%		1525 Å		
Standard deviation	± 0.15%	± 0.15%		± 9.2 Å		
Percentage deviation				± 0.6%		

of thickness and chemical composition could be obtained experimentally as was expected from the thoeretical considerations. For this purpose, twenty-five bits of 1 cm diameter were placed on the area of a substrate, as shown in Fig. 9. The output voltage E_0 was measured for each bit. The bits shown with arrows were also analyzed by X-ray fluorescence techniques.

A typical data sheet is given in Table III which is arranged in the same manner as Table I. From this table, it is seen that the chemical composition varies from only 20.2 per cent Fe to 20.7 per cent Fe. This corresponds to a standard deviation of as little as ± 0.15 per cent. The thickness variation is as small, 1510–1540 Å, with a standard deviation of ± 9 Å equal to ± 0.6 per cent. These variations are even smaller than were expected from a theoretical point of view. The distribution of chemical composition and thickness is random within the precision of the present methods of investigation.

In the densitometer assembly, the transmission of light through an evaporated film is measured by a photomultiplier. Since the transmissivity is an exponential function of the film thickness, a linear dependence of the transmission of light through the film (represented by the photomultiplier current) on the evaporation time should be obtained on a semi-logarithmic plot (Fig. 10), provided that the rate of evaporation was constant. As can be seen from Fig. 10, this is true for this evaporation. A few experimental points deviate from the straight line. This is caused by small changes in the ring source current. For a good current regulation, practically no deviation from the straight line can be observed—the rate of evaporation is constant.

Summary and conclusions

The results of the experiments described above may be summarized as follows (cf. Table IV).

The crucible yields an evaporation characteristic of the expected shape. Over a fairly short distance from the point above the center of the crucible, the decline in thickness is small, but beyond this a rather steep slope is observed. If a small thickness variation is required, the distance between source and substrate must be large compared with the diagonal of the substrate, and this results in a fairly low deposition rate. The shape of the curve in Fig. 6 can be explained by the source characteristic. The chemical distribution is random, the standard deviation is surprisingly small.

TABLE IV

Comparison between Crucible and Ring Source

	Crucible	Ring source
Substrate area (area covered by bits) (mm^2)	67×70 (4680 mm^2)	75×112 (8400 mm^2)
Maximum variation of chemical composition	0.6%	0.5%
Standard deviation of chemical composition	± 0.2%	± 0.15%
Percentage variation of thickness	± 5.1%	± 0.6%
Rate of evaporation for the present setup	3 to 12 Å/sec	Approx. 3 Å/sec

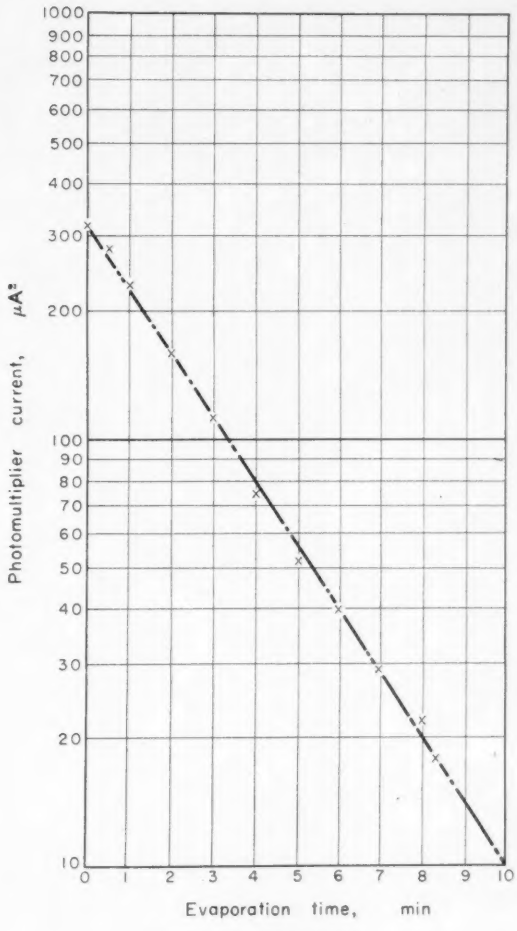

FIG. 10. Densitometer curve.

The evaporation characteristics of the ring source are as uniform as theoretically expected. Even for a substrate area that was twice as large as the one used for the crucible investigation, the variations in chemical composition and especially in thickness were smaller than in the case of the crucible.

For the practical application, it may be said that, in the case of the ring source, there is no danger of contamination by a support, while the slag formation is a serious disadvantage of the crucible technique. The slag also makes it difficult to maintain a uniform rate of evaporation, while the ring source is easily controlled in this respect. In the case of the crucible, it is important that the position of the crucible be fixed, since, otherwise, the deposition characteristic will

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be changed. In its present form, the ring source has two main disadvantages: the composition of the evaporated film depends greatly on evaporation temperature and time. Besides, the rate of evaporation is low. It may be possible, however, to overcome these disadvantages by developing new types of ring sources.

Acknowledgements

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Leak Testing of Large Welded Vacuum Vessels

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Principles and procedures are described for leak testing welded tanks of the vacuum powder insulated type intended for the storage of liquid oxygen and liquid nitrogen. Leak detection methods were employed firstly for checking individual sections of weld during manufacture, and secondly, for testing completed vessels. For the former, simple vacuum boxes were developed which could be attached temporarily to a section of welded plate and used in conjunction with a mass spectrometer leak detector to test various lengths of weld. Completed vessels were evacuated to a pressure of approximately one micron by a pumping system to which the leak detector was connected at a suitable point. The factors requiring consideration in order to ensure adequate leak detection sensitivity in all phases of the leak testing are discussed. Whilst the procedures adopted in the tests are related specifically to the particular application described, the principles involved are applicable generally to the leak testing of large welded vacuum vessels.

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Introduction

During recent years, methods for the detection and location of leaks in vacuum systems have advanced considerably and a variety of techniques and equipment, based upon well established principles, is now available to cope with most circumstances encountered in practice. The factors which determine the choice of a particular leak detection method have been reviewed on a number of occasions in the literature[1, 2, 3] and need not be reiterated here. Similarly, methods of employing the various types of leak detectors to optimum advantage are generally well known and for many applications the procedures are now routine. Sometimes however, a situation arises which calls for special consideration and may demand the development of new techniques or the modification of standard procedures in order to meet particular requirements. The present paper deals with such a case, in which the large size of the vacuum vessel and the necessity for carrying out leak tests on it during manufacture posed problems outside those normally encountered. Whilst the considerations to be discussed are related specifically to the particular application in hand, it is believed that the principles involved are generally applicable to the leak testing of large welded vacuum vessels.

The problem arose during the manufacture of tanks of the vacuum powder insulated type for the storage of liquid oxygen and liquid nitrogen. Each tank has a capacity of approximately 2750 cu. ft (7.8×10^4 l.) and comprises a cylindrical inner vessel constructed from welded stainless steel plate and a mild steel outer shell. The overall dimensions of a tank are approximately 48 ft in length and 11 ft in diameter. The annular space between the two vessels (ca. 1690 cu. ft in volume) contains thermal insulating powder and is evacuated and maintained during use at a pressure of not more than 10^{-2} Torr (10 microns).

After construction but prior to filling the annular space with insulating powder each tank was required to meet a static vacuum test in which the inner vessel was pressurized to 45 p.s.i. gauge and the annular space was evacuated to a pressure of 10 microns or less. Under these conditions, the maximum permissible pressure rise in the annulus was 24 μ over a 48 hr test period.

In view of the lack of previous experience by the manufacturers in construction of vessels of this type and size, and the somewhat stringent requirements on materials and welding procedures for the inner vessel to meet the severe service conditions, it was considered advisable (at least for the first tank) to carry out leak tests on each individual weld or group of welds during the course of construction. The leak testing procedures required therefore fell into two categories : (a) those to be carried out on sections of the inner and outer vessels during fabrication, and (b) tests on completed vessels.

Sensitivity required for leak detection

The specification of a maximum average pressure rise of 0.5 μ/hr in an annular volume of 1690 cu. ft (47.8×10^3 l.) corresponds to a maximum permissible leak rate for the annulus of the tank of 6.7 μl/sec. The question arises as to a rational distribution of allowable leakage for the inner and outer vessels of the tank, bearing in mind that for the static vacuum test the walls of the outer and inner vessels are subjected to pressure differentials of one and four atmospheres respectively.

Since the total lengths of weld for an inner and outer vessel are approximately equal (600 ft) and because the inner vessel was evacuated and leak tested prior to insertion in the outer shell, it was decided to apportion the permissible leakage equally between the two vessels *under similar conditions of test*. On the assumption that the leaks, if any, are predominantly viscous in character and hence proportional to the square of the pressure differential, it follows that the maximum permissible leakage for an inner vessel when evacuated was approximately 0.4 μl/sec.

For purposes of analysis, it was further assumed (i) that any leaks in either vessel would be confined to welds or demountable seals, i.e. that the steel plate itself was free from porous flaws, (ii) in the worst case, leaks might be distributed uniformly throughout the welds. On this basis, the maximum permissible leak rate/ft of weld was 6.7×10^{-4} μl/sec or 8.7×10^{-7} standard cc/sec. As will be shown later, under these conditions, if a length of 1 ft of weld is to be checked for leakage, the leak detection equipment must have a sensitivity under the conditions of use $\sim 10^{-8}$ std. cc/sec. A mass spectrometer type of leak detector was therefore imperative.

Leak detection on sections of weld

General considerations

As stated previously, means were required for testing any individual section of weld for leakage on both inner and outer vessels during the course of manufacture. (Where possible, welds were also checked for flaws by conventional radiographic methods.) The types of welds encountered may be classified into five main sections (see Figs. 5 and 6).

(i) and (ii) longitudinal and circumferential welds respectively on the cylindrical sections of the vessels,

(iii) *T* junctions between longitudinal and circumferential welds,

(iv) curved sections of welds on the dished ends of the vessels,

(v) welds around manholes and pipe entries into the inner and outer vessels.

The principle of test adopted is illustrated schematically in Fig. 1. A vacuum box *A*, which covered temporarily

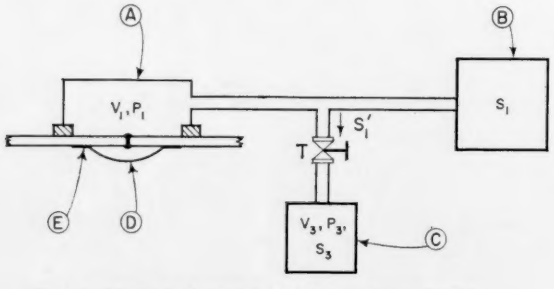

FIG. 1. Method adopted for testing sections of weld.

the section of weld under test, was evacuated by a pump *B* and also connected to the mass spectrometer leak detector *C*. An atmosphere of helium, at roughly atmospheric pressure, was maintained on the opposite side of the weld under a cover of sheet polythene *D*, fastened at its edges to the steel plate by suitable adhesive tape *E*. If a leak were detected, it could be located by reducing progressively the length of the helium envelope and finally isolated by a fine helium probe.

Vacuum required in the box

Before detailed consideration could be given to the design of suitable vacuum boxes, it was necessary to estimate the degree of vacuum required in a box to ensure sufficient leak detection sensitivity.

As shown in the Appendix, the build-up of helium L_3 in the analyser of the leak detector after time t is related to a leak L_1 in a weld by the expression :

$$L_3 = \frac{L_1}{1 + (P_1S_1/P_3S_3)} \cdot \frac{[1 - \exp\{-K_1(S_1 + S_1')t/V_1\}]}{[1 - \exp(-K_3S_3\,t/V_3)]} \quad (1)$$

where $V_1, P_1 \equiv$ volume and pressure respectively of the box,
$V_3, P_3 \equiv$ volume and pressure of the analyser of the leak detector,
$K_1S_1 \equiv$ speed of the roughing pump for helium at the box,
$K_3S_3 \equiv$ pumping speed for helium at the analyser of the leak detector,
$S_1' \equiv$ speed of the leak detector on the box side of the throttle valve *T*.

Since the response times for such a system are short (~sec), equilibrium is established quickly and in this case :

$$L_3 = L_1/[1 + (P_1S_1/P_3S_3)] \quad (2)$$

Now it has already been noted that for 1 ft of weld, the maximum permitted leak $= 6.7 \times 10^{-4}$ μl/sec of air. For helium this will be increased[1] by a factor varying between unity for large leaks and about 2.2 for small leaks $\sim 10^{-5}$ μl/sec. Hence, let us take L_1 for helium $= 10^{-3}$ μl/sec or 1.3×10^{-6} std. cc/sec.

Assigning reasonable values of $S_1 = 2$ l/sec, $S_3 = 20$ l/sec, P_3 (max.) $= 0.1$ μ, leads to the relations given in Table I.

TABLE I

Relation between pressure P_1 in the vacuum box and build up of helium L_3 in the leak detector

P_1 (μ)	L_3 (std. cc/sec)
1	6.5×10^{-7}
10	1.2×10^{-7}
50	2.5×10^{-8}
100	1.3×10^{-8}
500	2.6×10^{-9}
1000	1.3×10^{-9}

Modern mass spectrometer leak detectors are capable of a sensitivity $\sim 10^{-10}$ std. cc/sec for a signal to noise ratio of unity. On this basis a pressure of 1000 μ in the box should be sufficiently low to give a significant detector response for leaks of threshold importance in 1 ft of weld. In order to provide a reasonable safety factor however (e.g. for

possible increases in leakage when the vessel contains liquid oxygen or liquid nitrogen[6]) it is better to aim at a box pressure of 100 μ or lower.

The vacuum boxes

The major design requirements for the vacuum boxes may be summarized as follows :

(a) the working pressure in a box should not exceed ~100 μ ;

(b) attachment of a box to any welded section should be an easy, reliable and relatively rapid process ;

(c) the design should aim for a minimum number of different types and sizes of box to cope with all the five main types of weld listed previously.

The principal difficulty in meeting these requirements lay in making a satisfactory seal between the box and the section of the vessel under test. The surface of the steel plate was pitted and generally had a poor finish compared with normal vacuum engineering standards. Furthermore, the welds were approximately $\frac{1}{2}$ in. in width $\times$ 1/16 in. in height and imposed a relatively abrupt change in contour on the seal where the two ends of the box crossed the weld.

The method adopted, which proved satisfactory in operation, is illustrated schematically in Fig. 2. The vacuum box consisted of a flexible metal plate *A*, to which were cemented two rectangular rubber gaskets *B* and *C*. These gaskets, $\frac{1}{2} \times \frac{1}{2}$ in. in section, were made from non-interconnecting cellular (" microcel ") rubber. This material provided sufficient sponginess to effect a satisfactory seal with the steel plate *D*, and across the weld *E*, but at the same time was non-porous. The section of the box inside the inner gasket was connected via flexible neoprene hose to the leak detector *F*, which also contained the roughing pump ($2\frac{1}{2}$ l/sec displacement) for evacuating this volume. The annular

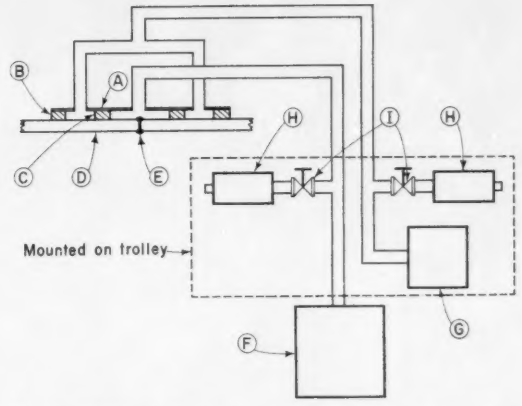

FIG. 2. Schematic illustration of the use of a vacuum box.

space between the two gaskets was connected to a second rotary pump *G*, of $2\frac{1}{2}$ l/sec displacement. By this means, leakage across the inner gasket was reduced sufficiently so that the inner volume of the box could be maintained at a pressure in most cases, of about 50 μ. For releasing the box from the welded plate after a leak test, air was admitted to each section of the box through driers *H* and inlet valves *I*. For transportability and convenience in use, the rotary pump *G* and the air inlet system were mounted on a trolley. Fig. 3 shows the complete equipment with a long box attached to a section of experimental welded plate (not part of a vessel). Another shorter box, seated on top of the trolley, is included to illustrate the rubber gaskets.

Two sizes of boxes enabled tests to be undertaken if required, on all welds on both inner and outer vessels, with the exception of manholes and pipe entries : (i) a box of overall dimensions 52 $\times$ $6\frac{1}{2}$ in., (ii) another box of dimensions

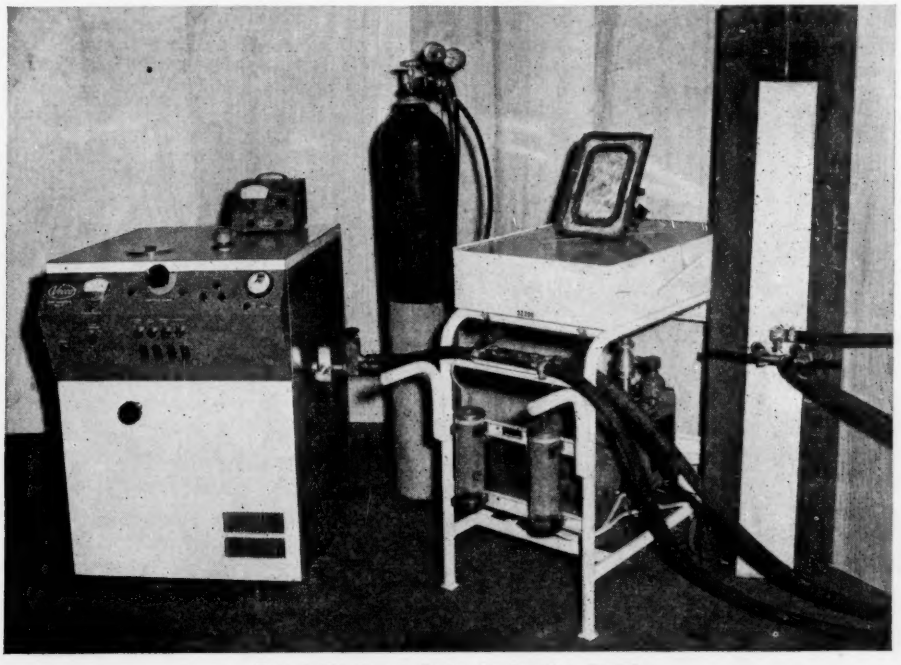

FIG. 3. Equipment for testing lengths of weld.

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14 × 9 in. These sizes covered test lengths of weld of 4 ft and 10 in. respectively and were chosen to suit the dimensions of the strakes of the vessels. The same long box was used to check both flat longitudinal welds and curved circumferential welds on cylindrical sections of both vessels. It was for this purpose that the top plate *A* (Fig. 2) of the box was made sufficiently flexible to conform to the 4 ft 6 in. radius of curvature for circumferential welds on the inner vessel. At the same time the plate had to be rigid enough to withstand the atmospheric thrust without undue distortion. Sheet brass of 16 S.W.G. was found to be satisfactory for this purpose. A short box was used to check T-junctions between longitudinal and circumferential welds. In this case however, due to its shorter length and greater width, the plate was too rigid to bend elastically to the required curvature. In consequence, the plate was preformed to a 4 ft 6 in. radius of curvature prior to the bonding to it of the rubber gaskets. This curvature, together with the sponginess of the gaskets enabled the same box to be used for both inner and outer vessels. For the dished ends of the vessels, combinations of flat or preformed long and short boxes enabled all welds to be tested.

The average time for a routine leak test using one of these boxes, including the time for evacuation, fastening of the polythene hood to the plate and filling it with helium, was approximately five minutes. If a leak were found in a section, this time was extended (to locate the leak) by an amount depending upon the length of weld under test and the magnitude of the leak.

For circular welds around manholes and pipe entries, three other boxes were employed, similar in principle to the rectangular type described above, but circular in section and preformed to fit the shape of the vessel at the required position.

Leak detection on completed vessels

The inner vessel

In addition to the tests just described, it was decided for two main reasons to test the inner vessel for leakage prior to insertion in the outer shell : firstly, in accordance with normal boiler code practice, the specification required a hydrostatic pressure test to be carried out on the completed inner vessel at 1.5 times the design pressure, i.e. 90 p.s.i. This may have caused small leaks to develop in welded sections. Secondly, because of the difficulties of locating and repairing any defects in the inner vessel once it had been assembled in the outer shell, any leaks should be detected and sealed at as early a stage as possible.

The maximum permissible leakage of 0.4 μl/sec quoted previously for the inner vessel when evacuated corresponds to a rate of pressure rise of only 0.018 μ/hr. It was therefore not practicable to carry out a static vacuum test on the vessel to check for leakage. In consequence standard practice was adopted, the vessel being exhausted by a pumping system to which the leak detector was connected at a suitable point. Whilst the vessel was being evacuated, all welds were covered with polythene hoods, and when a sufficiently low pressure had been obtained, leak detection was carried out progressively on the welds. In applying this technique however, there are a number of important considerations which need to be determined beforehand, in order to ensure that no significant leaks will remain undetected. These factors are outlined in the next two sections.

Leak detection sensitivity

The inner vessel was evacuated by a pumping system comprising a high speed vapour pump backed by rotary pumps. Consider the case of the leak detector connected to the system between the vapour and rotary pumps. As shown in the Appendix, the build-up of helium L_3 in the leak detector after time t is related to a leak L_1, in the vessel by

$$L_3 = \frac{L_1}{1 + (P_2S_2/P_3S_3)} [1 - \exp(-K_1S_1 t/V_1)] \quad (3)$$

where V_1 ≡ volume of the vessel
K_1S_1 ≡ speed of the vapour pump to helium at the vessel
P_2, P_3 ≡ pressures in the backing space and in the analyser of the leak detector respectively
S_2, S_3 ≡ pumping speeds in the backing space and leak detector respectively

Since the helium concentration C in the analyser of the leak detector $= L_3/P_3K_3S_3$,

$$C = \frac{L_1}{K_3(P_3S_3 + P_2S_2)} [1 - \exp(-K_1S_1 t/V_1)]$$

where $K_3 \equiv$ ratio of pumping speeds of the leak detector to helium and to air. If P_1 is sufficiently low for molecular flow in the vessel, $K_1 = K_3$.

Since $P_1S_1 \simeq P_2S_2$ and $P_3S_3 \ll P_2S_2$, we may write

$$C = (L_1/P_1K_1S_1)[1 - \exp(-K_1S_1 t/V_1)] \quad (4)$$

Now, if l ≡ total length of weld in the vessel
x ≡ length of weld exposed to helium
R ≡ maximum permissible leakage at 1 atm. pressure
k ≡ ratio of helium/air flow through the leak
$L_1 = (x/l)kR$

Hence

$$x = CK_1S_1 \left(\frac{l}{kR}\right) \frac{P_1}{[1 - \exp(-K_1S_1 t/V_1)]} \quad (5)$$

If the concentration C is taken as the minimum that is detectable by the leak detector, equation (5) thus gives the *minimum* length x which can be tested for leaks at any one time in terms of the other parameters of the system. Several important conclusions follow from this relation :

(i) For a given leak detector sensitivity C, pumping speed K_1S_1 and time for detection t, x is directly proportional to the pressure in the vessel.

(ii) The shortest length of weld that can be tested reduces as the time for detection increases, but is subject to the limiting value $x_{min} = CK_1S_1(l/kR)P_1$

(iii) Since at equilibrium $P_1 \simeq$ const./S_1, for a fixed leakage and outgassing in the vessel,

$$x = \text{const.}/[1 - \exp(-K_1S_1 t/V_1)].$$

i.e. for a given detection time, x reduces as S_1 increases.

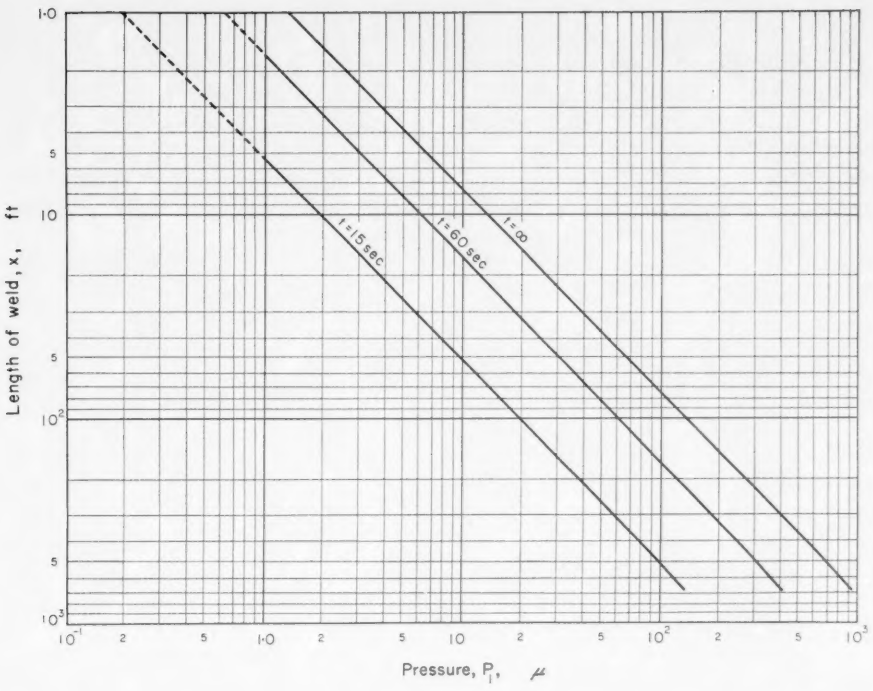

FIG. 4. Relation between minimum length of weld to be tested and pressure in the inner vessel. Pumping speed = 800 l/sec ; leak detector sensitivity = 1 part per million ; total leak rate = 0.4 μl/sec.

Conversely for a given length of weld to be examined, the time required for detection of a leak becomes shorter the faster the pumping speed for the vessel.

The above factors, together with economic considerations, thus determine the pumping system to be used.

For the inner vessel, $V_1 = 7.8 \times 10^4\, l$, $l = 600$ ft, $R = 0.4\ \mu$l/sec and a reasonable value for k is 1.6. Fig. 4 shows the relation between x and P_1 for various values of t, for a pumping speed for helium K_1S_1 of 800 l/sec and a leak detector sensitivity C of 1 part per million in concentration. Under these conditions, if the time for development of a threshold signal on the leak detector is set arbitrarily at, for example, one minute, the smallest length of weld that can be exposed to helium to ensure a significant response at a vessel pressure of 10 μ is 17 ft. This value can be reduced by increasing the time for the test (but only to a limiting value of 7½ ft) or by reducing the pressure in the vessel. Charts such as Fig. 4 are therefore a useful guide in determining initially the requirements for the pumping system and in ensuring that the tests undertaken can detect significant leaks. It should be remembered however, that the results obtained from such an analysis depend upon the initial assumptions. For example, the assumption of a uniform distribution of leaks throughout the total length of weld is a severe case unlikely to be encountered in practice. If it is found that the majority of the weld is leak free, the permissible leakage per foot for the remainder increases and correspondingly, the values of x for a given P_1 will be smaller than those shown in Fig. 4.

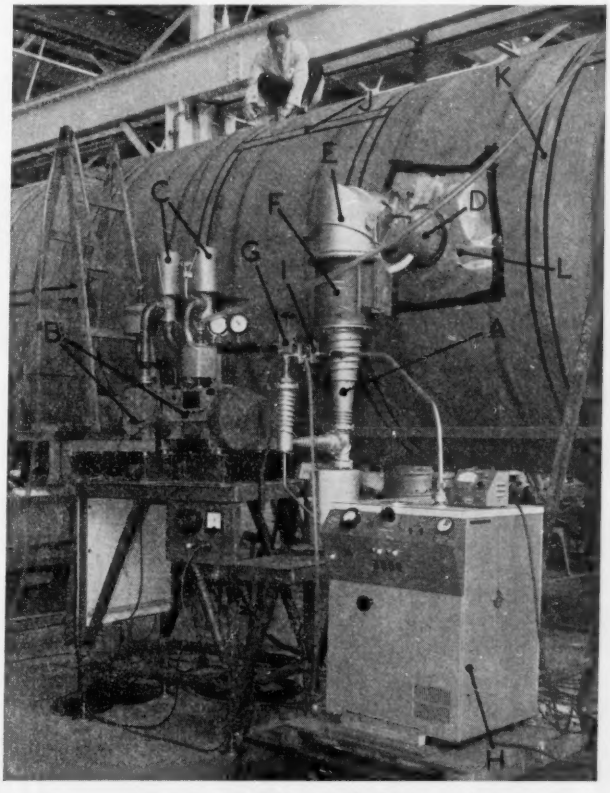

FIG. 5. Leak detection on the inner vessel.

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The pumping system

Considerations based upon those described above indicated that for reasonable response times and adequate sensitivity for leak detection, the pumping system should have a speed (to air) at the vessel ~500 l/sec and should reduce the pressure to about 1 micron or less. A booster type vapour pump was therefore selected.

Fig. 5 illustrates the equipment in use on the inner vessel. A booster pump *A*, with a peak speed of 800 l/sec was backed by two rotary pumps *B*, each of 7½ l/sec displacement, working in parallel. Two solenoid valves *C* protected the booster pump in the event of a power failure. The system was connected to the manhole on the vessel through a manifold *D* and an isolation valve *E*. A liquid nitrogen cold trap *F*, placed immediately above the booster pump, prevented backstreaming of pump oil into the vessel and also served as a high speed pump for vapours in the vessel. A window in the trap housing permitted the stainless steel ball containing the liquid nitrogen to be observed during pumping, so that, if necessary, the ball could be removed from the housing and replaced with a clean unit, after first allowing the pump to cool down and isolating it from the rest of the system by valves *E* and *G*. The leak detector *H* was connected to the backing side of the booster pump through a valve *I*. Attached to another part of the vessel, not shown in the photograph, were thermocouple vacuum gauges and a valve to which was connected a calibrated leak (~0.02 μl/sec) of the porous plug type.[4] This latter was incorporated to enable the magnitude of any leaks found in the vessel to be determined. Polythene hoods, such as *J*, *K* and *L*, to contain helium were fastened with adhesive tape to the vessel to cover all welds.

After the hydrostatic pressure test, but prior to evacuation, the inner walls of the vessel were very thoroughly cleaned and dried. This was mandatory in view of the end use of the vessel for the storage of liquid oxygen, but also served the additional purpose of accelerating pump-down and ensured that any leaks present would not be blocked temporarily by water.[5] This cleaning and drying procedure, together with the cold trap *F*, resulted in the experimentally observed pressure–time curve for the vessel during pump-down being close to that computed for an ideal system containing no vapour or adsorbed contaminants.

The complete tank

After the inner vessel had been assembled in the outer shell and pressurized to three atmospheres, the annulus was cleaned and dried and then evacuated with the same pumping and leak detection system as used for the inner vessel. Fig. 6 shows the equipment in use.

After reaching a pressure of approximately one micron or less, some welds which had been made after assembly, and which consequently had not been leak tested previously,

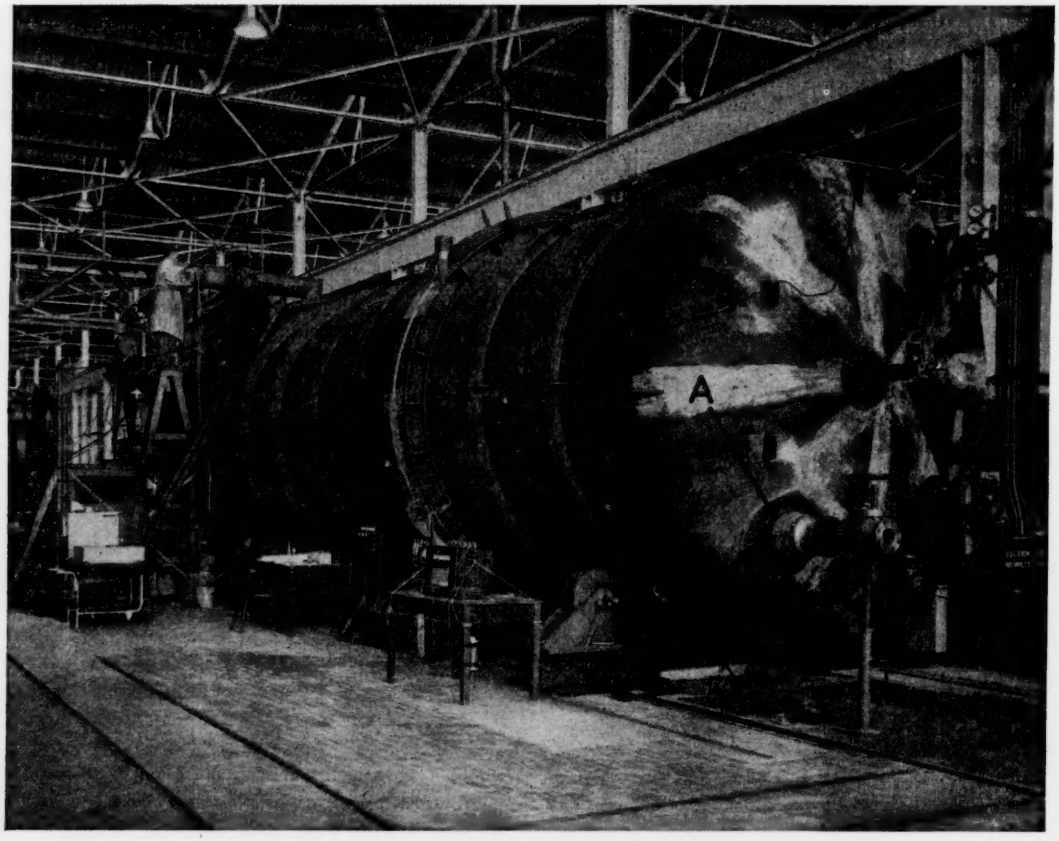

FIG. 6. Pumping and leak detection system in use on the outer vessel.

were covered with polythene and checked for leakage. In addition, as a final check on the inner vessel, a small quantity of helium, corresponding to 0.1 per cent concentration, was admitted to the pressurized vessel. The isolation valve E (Fig. 5) was closed for a given time to allow helium escaping through any leaks to accumulate in the annular space. The valve E was then opened and the leak detector observed for any response. Calculation indicated that for the helium concentration in the inner vessel mentioned above, and a pressure in the annulus of one micron, an accumulation time of approximately 100 sec was sufficient for the leak detector to respond to any significant leakage from the inner vessel.

If these leak tests for the inner and outer vessels proved satisfactory the static vacuum test was commenced. For this purpose the valve E (Fig. 5) was left open and the valve G closed, with the booster pump, of course, inoperative. The liquid nitrogen cold trap was therefore still connected to the annular space and so ensured that any pressure rise noted on the vacuum gauges was due to a real leak. Under these conditions it was found in practice that on a good tank no significant increase in pressure (i.e. $>1\ \mu$) could be detected over a 48 hr shut-down period.

On the first tank, leaks were found in some of the circular welds around the pant legs, such as A (Fig. 6), joining pipes to the outer vessel. Radiographic examination was difficult in such positions and had failed to detect any cracks. With the leak detection technique employed, it was found that by carefully and progressively reducing the length of weld covered with small strips of polythene, the positions of the cracks could be located positively to within $\frac{1}{4}$–$\frac{1}{2}$ in.

Finally, with the annulus still under vacuum and isolated from the pumping system, the inner vessel was partially filled with liquid oxygen. This cold test was undertaken principally to check that the vessel and piping would withstand rapid cooling without suffering structural damage. It did however, also indicate whether any minute leaks were significant in the vessel at low temperature which had not been detected in the previous tests at room temperature.[6]

Acknowledgements

The authors are indebted to Messrs. A. F. A. Harper and W. R. G. Kemp, National Standards Laboratory, Sydney, for considerable advice and assistance during the early stages of this work, and to many people in the Government Ordnance Factory, Maribyrnong for their help and cooperation in implementing the procedures described here.

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APPENDIX

Optimum Sampling Position for Leak Detector

When a vessel is exhausted by a pumping system comprising a high speed vapour pump and a rotary pump, the leak detector may be connected to the system on either the low or the high pressure side of the vapour pump. It is usually stated that the latter is the much more sensitive position. Whilst this is generally true, it is instructive to examine the conditions under which the increased sensitivity is obtained.

Consider a vessel of volume V_1, with a leak L_1, which is being exhausted by a vapour pump of speed S_1 at the vessel and a rotary pump of speed S_2 (Fig. A1). Let the pressures on the low and high pressure sides of the vapour pump be P_1 and P_2 respectively and the volume between the two pumps be V_2. The mass spectrometer leak detector may be connected (a) between V_1 and S_1, or (b) between S_1 and S_2. Let the volume and pumping speed at the analyser of the leak detector be V_3 and S_3. The throttle valve T is adjusted to give working pressures in the leak detector P_{3A} or P_{3B} for the two cases. The speed of the leak detector on the system side of the throttle valve is then S_1' or S_2'.

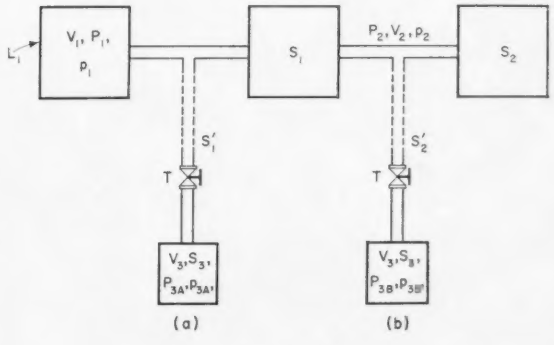

Fig. A1.

When helium enters the system through the Leak L_1, let the partial pressures of helium after time t in V_1, V_2, V_3 be p_1, p_2 and p_3 respectively.

Case A

If the pressure P_1 is sufficiently low for the gas flow in V_1 to be molecular

$$\begin{aligned} p_{3A}S_3 &= p_1S_1' \\ P_{3A}S_3 &= P_1S_1' \end{aligned} \tag{1}$$

From a consideration of the throughput of helium in the system, it follows that[1]

$$p_1 = \frac{L_1}{K_1(S_1 + S_1')}\,[1 - \exp\{-K_1(S_1 + S_1')\,t/V_1\}] \tag{2}$$

where K_1 is the ratio of the speeds to helium and to air. Similarly the build up of helium L_{3A} in the leak detector is given by

$$p_{3A} = \frac{L_{3A}}{K_3S_3}\,[1 - \exp(-K_3S_3\,t/V_3)] \tag{3}$$

From (1), (2) and (3) we obtain

$$L_{3A} = \frac{K_3}{K_1}\cdot\frac{L_1}{[1 + (P_1S_1/P_{3A}S_3)]} \times \frac{[1 - \exp\{-K_1(S_1 + S_1')\,t/V_1\}]}{[1 - \exp(-K_3S_3\,t/V_3)]} \tag{4}$$

Since in general, $K_1 = K_3$, $S_1' \ll S_1$, $S_1/V_1 \ll S_3/V_3$, equation (4) reduces to

$$L_{3A} \simeq \frac{L_1}{[1 + (P_1S_1/P_{3A}S_3)]}\,[1 - \exp(-K_1S_1t/V_1)] \tag{5}$$

Case B

In this case the gas flow into the throttle valve is viscous, but in the analyser of the leak detector it is molecular. Hence

$$\begin{aligned} p_{3B}K_3S_3 &= p_2K_2S_2' \\ P_{3B}S_3 &= P_2S_2' \end{aligned} \tag{6}$$

where[1] $K_3 \simeq 2.7$, $K_2 = 1$.

Also we have[1]

$$p_2 = \frac{L_1}{K_2(S_2 + S_2')}\,[1 - \exp\{-K_2(S_2 + S_2')\,t/V_2\}][1 - \exp(-K_1S_1t/V_1)] \tag{7}$$

$$p_{3B} = \frac{L_{3B}}{K_3S_3}\,[1 - \exp(-K_3S_3t/V_3)] \tag{8}$$

from (6), (7) and (8) it follows that

$$L_{3B} = \frac{L_1}{[1 + (P_2S_2/P_{3B}S_3)]} \times \frac{[1 - \exp\{-K_2(S_2 + S_2')\,t/V_2\}][1 - \exp(-K_1S_1t/V_1)]}{[1 - \exp(-K_3S_3t/V_3)]} \tag{9}$$

Since however $K_2 = 1$, and for most cases S_2/V_2 and S_3/V_3 are both large compared with S_1/V_1 this may be simplified to

$$L_{3B} \simeq \frac{L_1}{[1 + (P_2S_2/P_{3B}S_3)]}\,[1 - \exp(-K_1S_1t/V_1)] \tag{10}$$

Relative sensitivities

For a given leak L_1 in the vessel, it follows from equations (4) and (9) above, that the ratio of the sensitivities for the two positions of the leak detector is given by

$$\frac{L_{3B}}{L_{3A}} \simeq \left(\frac{P_{3B}}{P_{3A}}\right)\cdot\frac{P_{3A}S_3 + P_1S_1}{P_{3B}S_3 + P_2S_2}\,[1 - \exp\{-(S_2 + S_2')t/V_2\}]$$

Or since $P_1S_1 \simeq P_2S_2$, $P_{3A}S_3 \ll P_1S_1$ and $P_{3B}S_3 \ll P_2S_2$

$$\frac{L_{3B}}{L_{3A}} \simeq \frac{P_{3B}}{P_{3A}}\,[1 - \exp\{-(S_2 + S_2')\,t/V_2\}] \tag{11}$$

Now in most cases $(S_2 + S_2')/V_2 \gg S_1/V_1$. Hence after a time short compared with the response time for either of the two cases considered above

$$L_{3B}/L_{3A} \longrightarrow P_{3B}/P_{3A} \tag{12}$$

If the throttle valve T is therefore adjusted so that the pressure in the analyser of the leak detector is the same in both cases, no advantage is gained by connecting the leak detector to the backing side of the vapour pump. For small leaks however, it often happens that even with the throttle valve fully open, due to the impedance of the valve and the connecting line, the pressure P_{3A} obtained in the leak detector is well below the maximum permissible operating pressure, which is generally $\sim 10^{-4}$ Torr. In this case a considerable gain in sensitivity can be obtained by connecting the leak detector to the backing space and opening up the throttle valve until the pressure P_{3B} reaches the maximum permissible value.

Leakage within Glass-Fibre Reinforced Epoxy Resin Laminates

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During the test programme for the Harwell 7GeV Proton Synchrotron Vacuum Chamber, leaks were discovered within epoxy resin glass-fibre laminates. Successive steps were taken to locate the leaks and determine their nature. Initially, it is shown that their magnitude depends upon method of fabrication. Additionally, it is shown that hollow glass filaments which exist within the yarn of the cloth are also a contributory factor. Photographic evidence is presented in support of these findings.

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Investigation into the nature of leakage within laminates

In all cases samples were tested by using helium as a probe gas in conjunction with a mass spectrometer, which had a sensitivity of the order of 10^{-9} litre Torr/sec. Two modes of testing were employed. The first method is illustrated in Fig. 1(a). Each specimen was machined into a 6 in. diameter

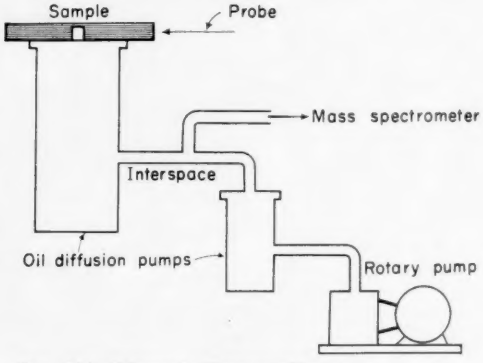


FIG. 1(a). Schematic diagram of leak test apparatus.

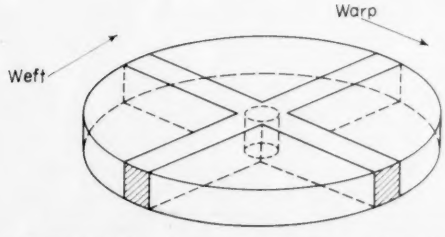


FIG. 1(b). Machined laminate showing leakage regions (shaded).

disc, and a blind hole drilled at its centre. The disc was placed centrally over a pumping system connected in turn to the spectrometer, and the probe gas was applied at the periphery of the sample. From the results of numerous tests the following observations were made :

(i) Leakage paths were evident wherever the directions of the weft and warp of the cloth were in line with the central (pumped) hole, i.e. four paths only were found in each sample (Fig. 1b).

(ii) Cross plying the cloth so that the weft (or warp) was at 45° to that of adjacent layers, produced eight leaks instead of four.

(iii) Leakage was not detected in samples of cast resin similarly tested.

(iv) Leakage was not detected through spliced samples (Fig. 2).

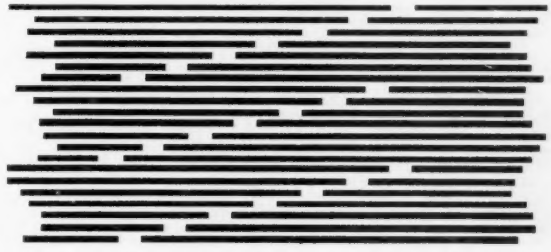


FIG. 2. Spliced laminate showing method of splicing.

The inference from these tests is that leakage is always associated with the directions of the cloth weave. That the particular geometric pattern of Fig. 1(b) is evident depends solely on the shape of the pumping aperture, and is irrespective of its position in the sample. It follows from this, that leakage paths occur at each point within the laminate in directions along the weave of the cloth to that point.

The cause of leakage may be due to one or more of the following :

(a) Lack of bonding, or bond failure, between the resin and glass fibres which may be due to inadequate cloth wetting by the resin, incompatibility of the resin with the particular glass-cloth finish, or separation of the cured resin from the cloth due to temperature stresses incurred during or after the curing cycle.

(b) Each bundle of fibres not being wetted through to the centre by the resin. This is not a likely cause if a reasonable wetting time is allowed since very high capillary forces are associated with bundles of such small fibres.

(c) Some of the individual fibres being hollow.

Further tests were carried out :

(v) Variation in cloth wetting time by the resin, curing conditions, and cooling time subsequent to cure, produced considerable variation in the size of leak detected. Glass cloth layers were immersed in resin for periods up to 5 days, cured, and slowly cooled. These samples contained the smallest measured leaks.

In spite of all subsequent variations of cloth finish, cure cycle and controlled slow cooling, it was always possible to detect a minimum size of leak in line with the weave, which could not be eradicated and suggested a leakage path independent of the conditions under which a laminate is made. This implied that leaks of type (a) and (b) had been substantially eliminated. Such a condition is fulfilled by hollow fibres within the yarn. The second method of test involved the use of a specimen as shown in Fig. 3, viz. a laminate 6 in. × 3 in. × $\frac{1}{4}$ in. with un-wetted glass cloth extending 30 in. beyond one edge. This sample utilized the full width of a 36 in. roll of cloth.

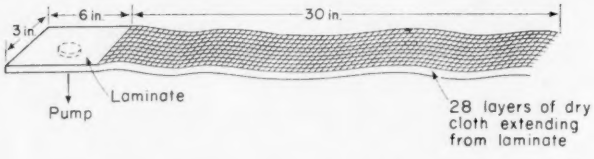


FIG. 3. Laminate with extended glass cloth.

(vi) With this sample it was possible to test the interfaces between resin and cloth. No leaks were found in this region which suggests compatibility of resin, finish and glass cloth for this specimen.

(vii) Tests for leakage were made along the dry cloth at the end remote from the laminate. Initially the ends of this cloth did not terminate in cut fibres, since the yarn was returned back and forth along the width in the weaving process. By enclosing the ends of fourteen layers of cloth and maintaining the enclosure filled with helium for 20 min, no leakage was recorded.

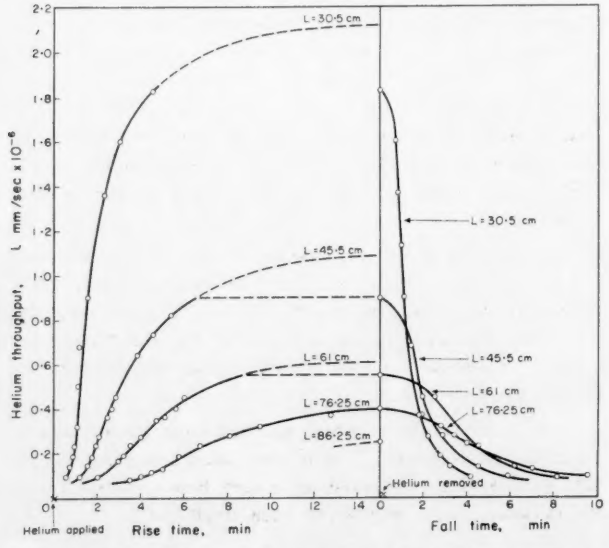


FIG. 4. Leakage variation with time for different leakage paths (*L*).

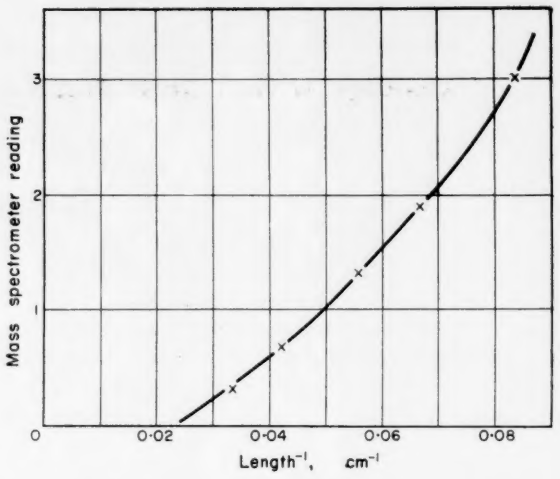


FIG. 5. Variation of throughput with length of glass fibre.

(viii) When the looped ends were cut and tested as in (vii), leakage was detected. The magnitude of leakage was then measured for various lengths of cloth. From the readings taken, Figs. 4 and 5 were plotted.

(ix) On isolating the cut ends from helium and extensively probing along the cloth no leakage was detected.

(x) To ensure helium was not travelling down the fibre bundles in (viii) (as opposed to the individual fibres) the short plies, perpendicular to the length, were removed over a 4 in. length of each layer (Fig. 6) and compressed air forced between the strands. The indication on the spectrometer remained constant throughout the experiment. In confirmation, the same 4 in. lengths of cloth were immersed in a liquid of low viscosity, viz. methanol, which readily penetrated the fibre bundles. Again the magnitude of the leakage remained constant during the experiment.

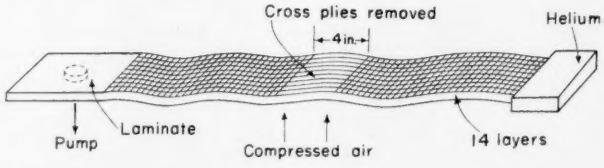


FIG. 6. Laminate with extended glass cloth, showing region of removal of cross plies.

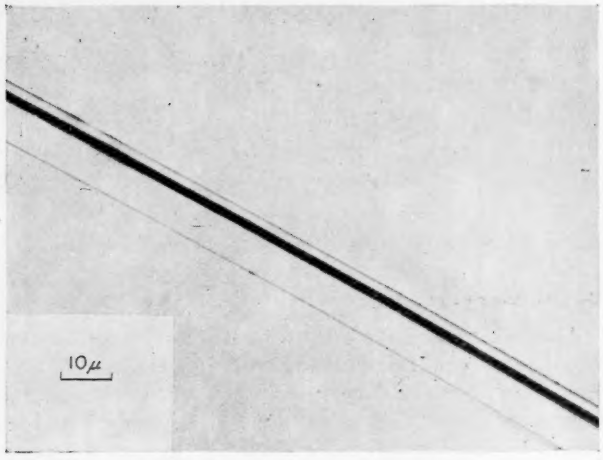
Photographic evidence

Specimens of the yarn, which contain 204 individual filaments, were combed out on a glass slide, to enable separate filaments to be seen. On inspection through a microscope (magnification 400) hollow filaments were found. It must be remarked that such filaments were found only by diligent searching, and the impression was formed that the hollow fibres were only a few per cent on the total number. On immersing the fibres in oil of refractive index similar to that

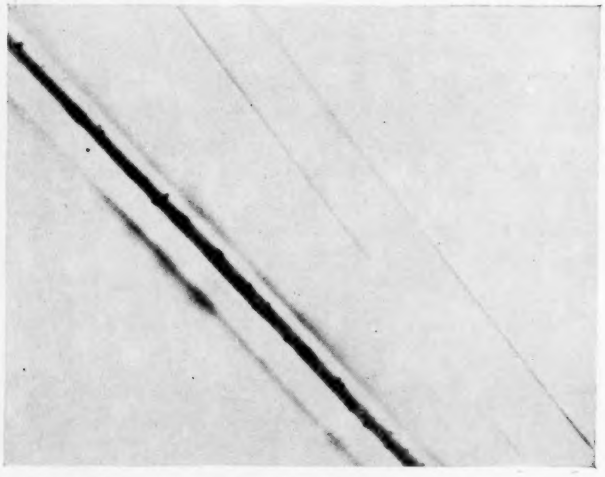
of glass the hollow centres could be observed and measured.

Further evidence was provided by the introduction of a strong solution of crystal violet dye in euparal into the capillaries.

Photographs were taken to record the above evidence (Fig. 7), the overall magnification being 1600. The nominal diameter of each filament is 10 μ while that of the observed capillaries is approximately 1.5 μ.



(i) Hollow filament (10μ) with 1.5μ bore.



(ii) Capillary containing crystal violet dye, and solid filament.

FIG. 7. Photographic evidence of hollow fibres.

Theoretical considerations

When helium was applied to the cut ends of the dry cloth extending 34 in. from the laminate (Fig. 3), some 3 min delay was encountered before a response was observed in the mass spectrometer. The response time for the instrument was approximately 1 sec when helium was allowed to enter the system through a calibrated leak adjacent to the laminate. The implication is that the leakage paths have a very high ratio of length to cross section. The time taken for the helium to reach the spectrometer and the subsequent increase in response was plotted (Fig. 4) for several different lengths of leakage path. The length was measured from the ends of the dry cloth to the pumping aperture in the laminate. The curves were extrapolated to the maximum leak rate and the result plotted against the reciprocal of the path length. Instead of a straight line graph passing through the origin, which would be consistent with flow through pipes of constant cross-section, Fig. 5 shows a curve extrapolated to cut the ordinate at a finite value. At this point, which corresponds to a length of glass cloth of some 116 cm, the conductance is zero. This indicates that capillaries of this length are the maximum likely to be encountered. From the increasing slope of the graph with decreasing length, it is evident that there are more leakage paths at the shorter lengths.

It is difficult to calculate accurately the percentage of hollow fibres, but it is interesting to evaluate results based on the following considerations.

(i) The quantity of gas per second passing through a capillary is given by[3, 4]:

$$Q\,L = 10^{-9}\left\{5.25\,\frac{\eta_{\text{air}}}{\eta}\,D^4 + 7.4\left(\frac{m_{\text{air}}}{m}\right)^{\frac{1}{2}} D^3 + 0.074\,\frac{m_{\text{air}}}{m}\,D^2 \log_e\left[1 + 24\left(\frac{m}{m_{\text{air}}}\right)\frac{\eta_{\text{air}}}{\eta}\,D\right]\right\} \qquad \text{(i)}$$

where Q is the throughput in litre Torr/sec
L capillary length (cm)
η_{air} air viscosity of air
η viscosity of helium
m_{air} molecular weight of air
m atomic weight of helium
D capillary diameter (μ)

One would expect a value of Q greater than that based on the assumption of purely molecular flow[4], viz.

$$Q = C\,P = \frac{12.1\,D^3}{L}\,P \qquad \text{(ii)}$$

since, viscous flow occurs at the end exposed to atmosphere. In fact that given by (i) is 2.5 times greater for the case considered.

(ii) From photographic evidence the average diameter of capillaries in the glass filaments observed is 1.5 μ. It is important to note that if the average diameter is greater than supposed, then the number of hollow fibres necessary to produce a given leak rate will fall rapidly since the conductance (assuming (i)) varies as the fourth power of the diameter.

By using (1) the throughput of a single capillary, was calculated for various lengths (column 2, Table I). In Fig. 4 the total throughput (litre Torr/sec) passing through the capillaries was extrapolated to its maximum (constant) value (column 3). Then by using assumption (ii) the number of hollow filaments was calculated for each test length (column 4).

From the knowledge of the diameter of the pumping aperture, the threads per inch of the cloth weft, the number of layers of cloth under test and the number of filaments in the yarn, the total number of filaments terminating at the

TABLE I

Glass cloth length (cm)	Calculated throughput of a single capillary of diam. 1.5μ (litre Torr/sec)	Total throughput of 14 layers (litre Torr/sec)	Number of hollow filaments	Number of hollow filaments (%)
30.5	2.49×10^{-9}	2.0×10^{-6}	804	2.34
45.75	1.66×10^{-9}	1.1×10^{-6}	670	1.95
61.0	1.24×10^{-9}	6.0×10^{-7}	484	1.41
76.25	1.0×10^{-9}	4.0×10^{-7}	400	1.17
86.25	8.8×10^{-10}	2.5×10^{-7}	284	0.83

pumping aperture was calculated to be 3.43×10^4. The number of hollow filaments expressed as a percentage is shown in column 5 of the Table.

Conclusions

Leaks within glass cloth laminates are dependent upon conditions under which specimens are prepared. Factors which contribute to leakage include, insufficient wetting of the cloth by the resin prior to cure, and shock cure conditions which tends to cause separation between resin and glass.

Even when care is taken to avoid the above conditions, leaks may still be found due to hollow filaments in the yarn of the cloth. From Fig. 8 the number of such paths decreases with increasing length. Extrapolation indicates that the longest paths are somewhat in excess of 1 m for the sample tested.

Approximate estimates indicate that the capillaries number a few per cent. Since no leaks were found when cut fibres are not exposed, it appears that the resin bonds satisfactorily to the glass.

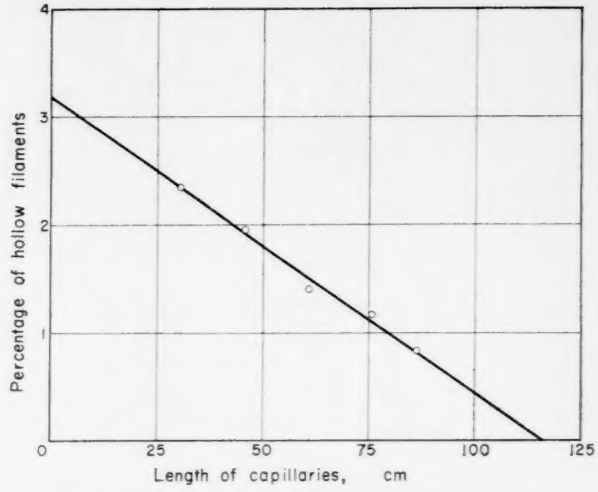


FIG. 8. Variation of number of hollow filaments with length.

Acknowledgements

Acknowledgement is made to the Director of the Atomic Energy Research Establishment and the Director of the Rutherford High Energy Laboratory for permission to publish this paper, and also to Mr. S. H. Cross in whose group the research was carried out, for his encouragement and many helpful discussions. Photographs were kindly supplied by Dr. J. R. K. Savage of the Medical Research Council.

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Lower Pressure Limit of Common Gauges*

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1. Introduction

Measuring lowest gas pressures is quite a difficult procedure. The practice of calibrating vacuum gauges against the McLeod gauge reference is certainly questionable in the lower range. I do not know of any other case where measuring devices are calibrated against only one absolute meter and then extrapolated over more than eight orders of magnitude. Unfortunately, we do not know all the effects that are involved. Even we are quite uncertain as to how much the effects we know contribute quantitatively.

The 85 year old McLeod compression manometer is still the only instrument that is absolute, but we can only measure with it gases that do not condense by the compression process. Compression ratios might be as high as $1 : 10^6$. All other high vacuum gauges are directly or indirectly calibrated against the McLeod.

The lower limit of the McLeod is mainly a technical limit, which depends on the cross section of the capillary, and how large the volume to be compressed (normally by mercury) can be made. The weight of the mercury becomes too great and the capillary forces become too high.

2. Definition of lower pressure limit

For the definition of the lower limit of pressure measurement, I would like to follow a suggestion of W. E. Dahlke and H. J. Schütze[1, 10]. They define the lower limit p_{min} for an ion gauge as that pressure where the error of measurement equals 10 per cent. It is easy to define such a limit, as it is difficult to determine its numerical value. Most of the lower limits given in company catalogues undoubtedly do not conform with this definition.

The McLeod manometer has its lower limit p_{min} as defined here, at about 10^{-5} Torr.

3. Mechanical gauges

All mechanical manometers that measure the gas pressure directly by the force of the gas molecules exerted on a membrane or meniscus exhibit a lower limit of around 10^{-3} Torr. There are many means for measuring the deflection of membranes, but at lower pressures there are effects which are very difficult to control. For example, capacitance micromanometers, at which vapor molecules with dipole momenta are absorbed, give quite erroneous pressure readings. I would say that any such mechanical manometer claiming a limit lower than 10^{-3} Torr does not comply with the general conditions.

4. Thermal conductivity gauges

Another typical example where the lower limit is quite uncertain is a vacuum gauge based on thermal conductivity. One of those is the Pirani gauge. In a thermal conductivity gauge, heat is normally introduced into the gauge by electrical energy, and the heat loss by conductivity through the gas is measured. There are also other heat losses, for example, radiation losses and conductivity losses through the support of the heated element. These losses determine the lower limit. The heat balance is simply expressed by :

$$Q_{total} = Q_{gas} + Q_{rad} + Q_{metal} \tag{1}$$

We may assume that Q_{gas} can still be determined with 10 per cent accuracy if its value is not less than 1 per cent of all other heat transported from the heated element. The lower limit is then given by :

$$Q_{gas} = 0.01\ (Q_{rad} + Q_{metal}) \tag{2}$$

For a simple heating element consisting of a wire of length l and radius r, we can roughly determine the lower limit by evaluating (2) and solving for p_{min} :

$$p_{min} = 0.01 \left(\frac{\pi\, m}{2\, k}\right)^{\frac{1}{2}} . T_1^{\frac{1}{2}} \times \left[\sigma (T_1^2 + T_2^2) . (T_1 + T_2) + 4\lambda \frac{r}{l^2}\right] \tag{3}$$

where m = mass of one gas molecule,

k = Boltzmann constant,

T_1, T_2 = ambient temperature and temperature of wire, respectively,

σ = radiation constant,

λ = heat conductivity coefficient.

We can always choose a wire of practical dimensions r and l, so that the expression $4 . \lambda\, r/l^2$ is negligible against the radiation part of the equation. Using, for example, a wire of $2r = 0.01$ cm and $l = 15$ cm, $\lambda = 0.1$ cal.deg^{-1}. cm^{-1}.sec^{-1}, $T_1 = 273$ °K, and $T_2 = 373$ °K, we arrive at $p_{min} = 8 \times 10^{-4}$ Torr, which is for most thermal conductivity gauges a realistic lower limit as defined in this paper.

*Paper given on invitation of the American Vacuum Society during the Panel Discussion at the 7th National Symposium on Vacuum Technology, 12 October, 1960.

5. Viscosity type gauges

In the same pressure range where the thermal conductivity gauges work, viscosity is a function of pressure too. For the few existing gauges working on this principle the lower limit is of the same order of magnitude. Instead of heat, mechanical energy is induced into a system capable of vibration. The damping is measured by determining the "half-time." In recently developed mechanical systems[2], measurements are made of amplitudes at resonant frequencies, or of the energy necessary to keep such a device vibrating at a constant amplitude. The lower limit is determined by the fact that the damping results more and more from other causes that do not depend on the gas pressure, as for example, mechanical damping of the system itself. It lies in the same order of magnitude as the lower limit of the heat conductivity gauges.

6. Radiometer type gauges (Knudsen gauges)

Although the radiometer type gauges (Knudsen gauges) have not yet left the laboratory stage, I would like to draw some attention to this type, especially since this is the only high vacuum-gauge that indicates the pressure of any gas or vapor independent of its kind. It should be possible to develop it to an absolute gauge. This is only true as long as the accommodation coefficients of the cold and hot parts of the gauge are equal.

Knudsen and others gave a complete theory of this gauge, which may be condensed into the following formulas, where F is the force on the colder plate of temperature T_1 originating from molecules coming from the hotter plate of temperature T_2 (see Fig. 1).

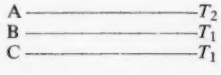


FIG. 1. Schematics of radiometer type gauges.

$$F = \tfrac{1}{2} k_1 \,.\, k_2 \,.\, p \,.\, \left(\sqrt{\frac{T_2}{T_1}} - 1\right) \tag{4}$$

$$k_1 = 1 + \frac{\alpha_2 - \alpha_1}{\alpha_1 + \alpha_2 - \alpha_1 \,.\, \alpha_2} \tag{5}$$

$$k_2 = \frac{1}{\pi}\left[\frac{2 \,.\, (1 + \frac{d^2}{b^2}) \,.\, b^2 - d^2}{b^2 \,.\, (1 + \frac{d^2}{b^2})^{\frac{1}{2}}} - \frac{d}{b}\right] \,.\, \text{arc tan}\, \frac{b}{d} \tag{6}$$

where $\alpha_{1,2}$ = accommodation coefficients

in general: $\alpha = \dfrac{\overline{E_i} - \overline{E_r}}{\overline{E_i} - \overline{E_T}}$

where $\overline{E_i}$ = mean energy of incident molecules,

$\overline{E_r}$ = mean energy of reflected molecules,

$\overline{E_T}$ = thermal energy corresponding to the surface temperature T,

d = distance between plates,

b^2 = dimensions of surface.

The system can mathematically be treated in the same way as a mirror galvanometer. The lower limit is thus determined by the mechanical constants of the torsion system and its stability. In a cylindrically symmetric system developed by H. Klumb and H. Schwarz[3] the practical lower limit lies at a "reduction factor" 10^{-8} Torr . m^{-1} . mm^{-1}. This means 10^{-8} Torr for 1 mm deflection on the scale in 1000 mm of distance from the mirror, using a tungsten wire of 0.01 mm diameter, cooling with liquid nitrogen and heating the hot part to $T_2 = +350°C$.

A recent proposal[4] of a resonance Knudsen gauge (see Fig. 2) might lead to the ultra high vacuum range. In this

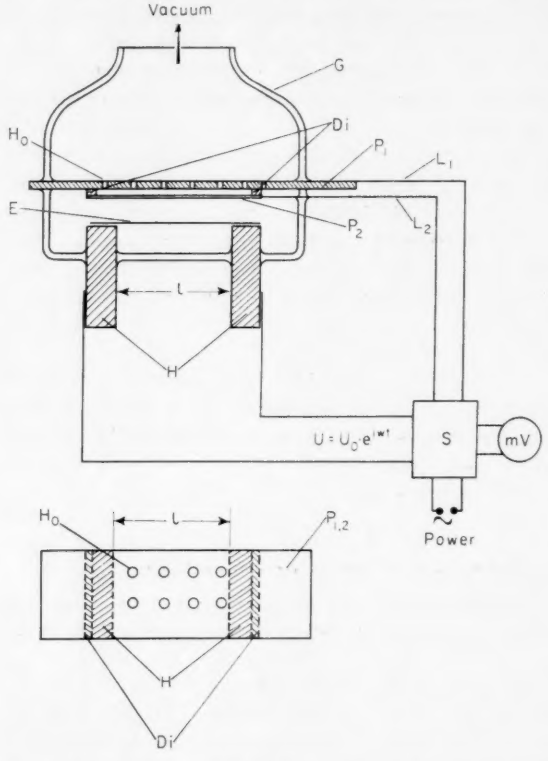


FIG. 2. Schematic drawing of device for measuring low gas pressures by forced periodic changes of kinetic energy of gas molecules. (H. Schwarz[4]).

system the mechanical damping is reduced to its minimum by having the movable member P_2 vibrate at its resonant frequency, while this member receives the radiometric force periodically at the same frequency. It will be difficult to get a commercial Knudsen gauge, but here exists the possibility to obtain another absolute gauge besides the McLeod for the low pressure range. The uncertainty of the lower limit of all other high vacuum gauges might then be cleared up somewhat.

7. Ionization gauge

The gauge used mostly today in the low pressure range is the ionization gauge. In principle it is the easiest to handle, since only electronics are involved. However, the gas molecules that indicate the pressure have to suffer quite an

attack, as they have to be ionized by electron impact. This fact, plus the presence of charged particles, electrons, as well as positive and negative ions, excited molecules, excited atoms, excited ions, damaged molecules, radiation of quite a variety of wavelengths down to soft X-rays, the presence of electrical fields originating from electrodes and uncontrolled changes at surfaces[5] and within the space, and absorption and desorption effects[5], indicate the complexity of the problem. In gauges with hot filaments, the presence of the hot surface introduces still more problems. I would like to divide the effects that determine the lower limit of the ion gauge into two groups :

Group I—Those effects that are due to the internal physics and chemistry of the ionization tube.

Group II—Those effects that are due to external conditions.

Group I

1. X-rays generated at the acceleration electrodes for the electrons.
2. Electron emission of the ion collector.
3. Formation of negative ions, especially with the very slow electrons existing in the magnetron and Penning type gauges.
4. Absorption and desorption processes and gas exchange[5] (see Figs. 3 and 4).

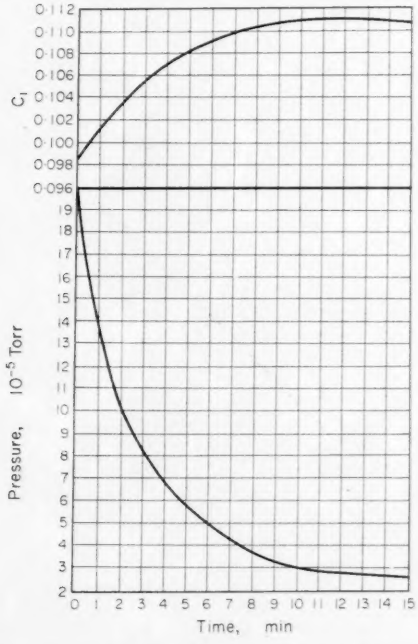


FIG. 3. Gas exchange in a normal ionization gauge during continuous operation ; at the beginning argon in the volume and nitrogen in or on the surfaces ; C_1—ionization gauge constant as calculated from : $p = C_1 \cdot i^+/i^-$, p—measured in Torr by Klumb-Schwarz radiometer gauge[3]. (H. Schwarz[5]).

5. Change of electrical fields by wall charges[5] and space charges.
6. Barkhausen–Kurtz oscillations, plasma oscillations, etc., varying with effects 3 to 5.

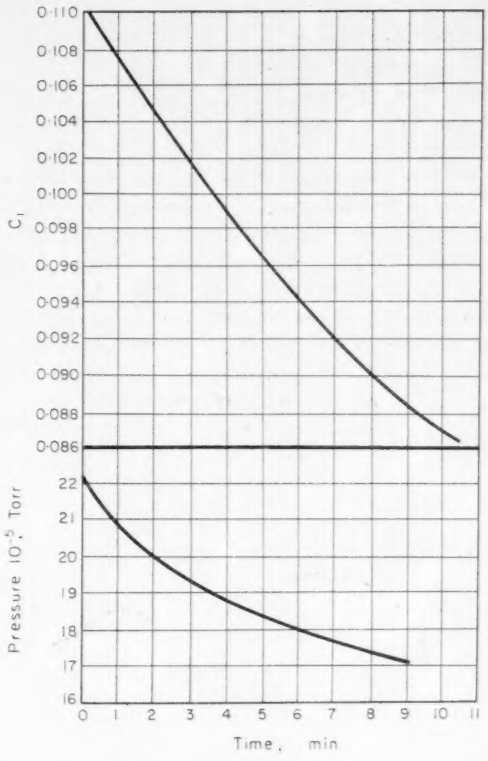


FIG. 4. Gas exchange in a normal ionization gauge during continuous operation ; at the beginning nitrogen in the volume and argon in or on the surfaces. (H. Schwarz[5]).

7. Effect of hot filament.
(a) Cracking large molecules like oil[5].
(b) Temperature ionization and excitation.
(c) Photons coming from light of hot filament generating photoelectrons at collector.
(d) Vapor pressure of filament material.
8. Unknown gas content at low pressure[5] which results in uncertainty of the ionization constant, e.g. the measurements of ionization gauges compared with Knudsen type gauges.

Figs. 3 and 4 represent measurements in a relatively small and closed volume consisting of a normal triode gauge and a radiometer type gauge as developed by H. Klumb and H. Schwarz[3]. In Fig. 3, measurements were taken in argon after the ion gauge had been operated in nitrogen until it had been saturated. The lower part shows the pressure drop with time ; the upper part the change of the ionization gauge constant C_1 as defined in $p = C_1 \cdot i^+/i^-$, where pressure p is measured in Torr, i^+, i^- are the ion current and electron current respectively.

C_1 has been calculated from the measured values of i^+, i^-, and p ; the latter measured with the Klumb–Schwarz vacuum gauge[3]. From the changes of C_1 it must be concluded that an exchange of gas took place between nitrogen previously absorbed by the surface and argon in the volume.

Fig. 4 shows an inverse experiment with nitrogen after previous long operation in argon.

Group II

1. Electrical leakage.
2. Gas permeability of walls.
3. Degree of outgassing.
4. Small tube connexion dependent on kind of gas or vapor.

Before 1940, most users of ion gauges thought that the lower limit of the ion gauge was given by the electronic circuitry, namely the limitation of measuring lowest currents to the ion collector. W. Nottingham[6] found that the current to the collector at low gas pressures was not any more proportional to the pressure, and he contributed this fact to the soft X-rays produced at the electrode which accelerates the electrons[7]. These photons, in turn, create photo-electrons at the ion collector. This, of course, simulates an ion collection. Bayard and Alpert[8] measured the curves as shown on Fig. 5 for a conventional ion gauge

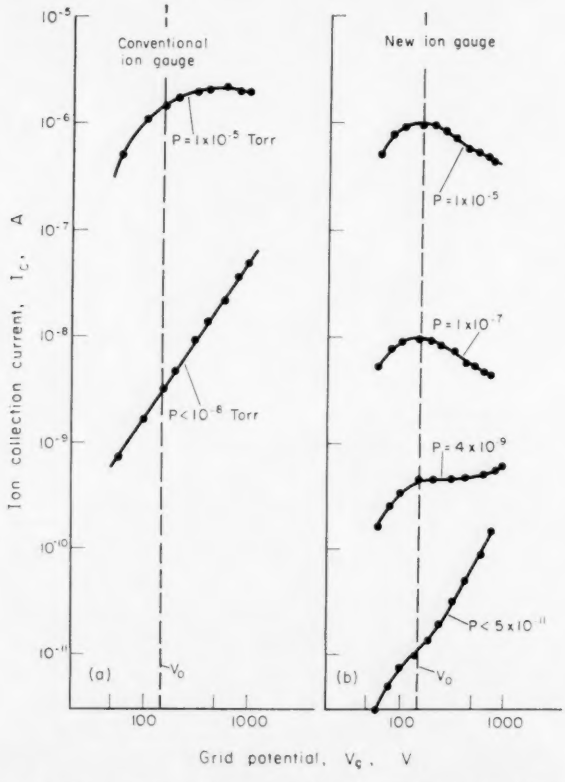


FIG. 5. X-ray effect in ionization gauges. (Bayard and Alpert[8]).

and for their newly developed gauge with a considerably smaller collector in order to reduce the surface exposed to the X-rays. The right side shows that in their gauge the X-ray photons are still small in number compared with the number of ions at pressures of the order of 10^{-9} Torr.

Another method to eliminate the X-ray effect had been proposed by G. G. Metson[9] applying a retarding field in front of the collector. An example is shown on Fig. 6 where E. Dahlke and H. J. Schütze[10] adjusted the screen grid potential in such a way that the lower limit p_{min} could be decreased by $3\frac{1}{2}$ orders of magnitude.

A third method as described and tested by E. Dahlke and H. J. Schütze[10], is the screening of the ion collector against X-rays, e.g. in a picture tube used as an ion gauge (see Fig.7). With suitable potentials at the electrodes, Dahlke

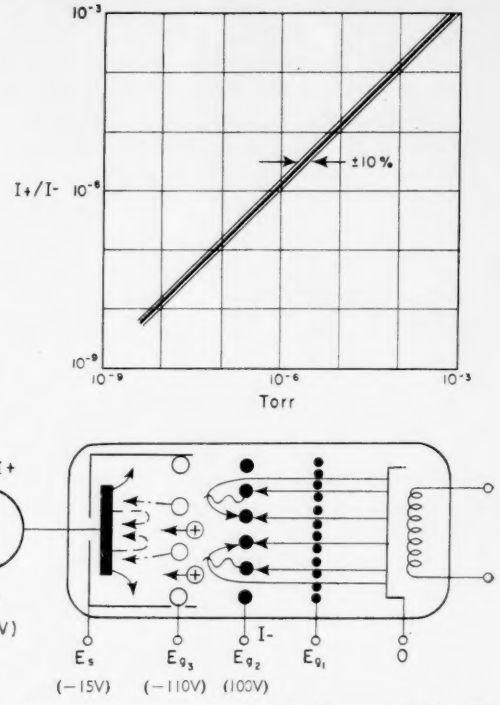
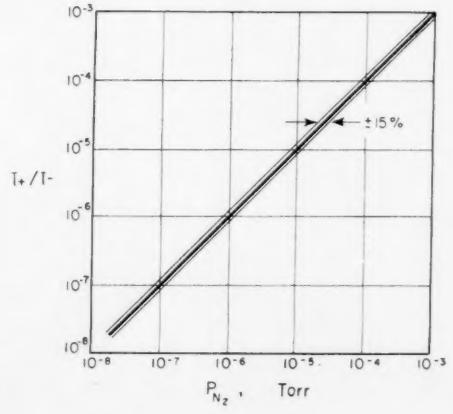
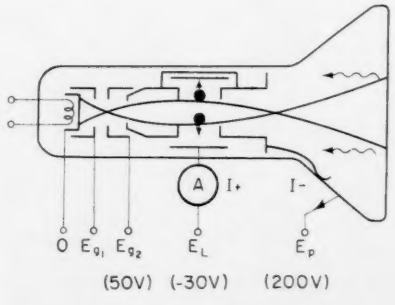


FIG. 6. Retarding field ionization gauge. (Dahlke and Schütze[10]).





Pressure measurement AW 53-88

FIG. 7. X-ray screening ionization gauge. (Dahlke and Schütze[10]).

and Schütze obtained p_{min} of less than 5×10^{-8} Torr. Fig. 8 gives an idea of the improvement in the lower limit of

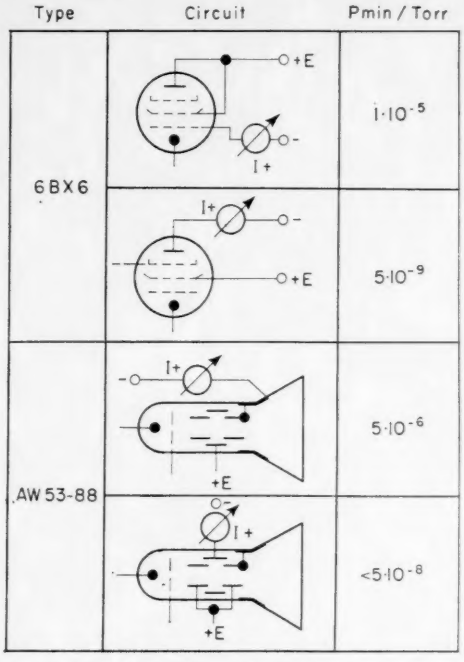


FIG. 8. Comparison of retarding field and X-ray screening ionization gauges. (Dahlke and Schütze[10]).

the two means for preventing the X-ray effect by a retarding field (tube 6B × 6) and screening (tube AW53 −88), as measured by E. Dahlke and H. J. Schütze. J. M. Lafferty[11] could reduce the X-ray effect by circulating a small number of electrons on a long spiral path such as in a magnetron, and obtaining a great number of ions without many electron impacts on the acceleration electrode. Along the same line of thinking is the ionization gauge developed by Houston[12] who claims to have reached a range lower than 2×10^{-12} Torr. In our own experience, we found a tremendous " pumping " action in this kind of ion gauge[5].

The next order of pressure limitation would be the equilibrium between the " pumping " action of the gauge and the permeability to helium of the pyrex glass wall which would mean a pressure minimum of approximately 10^{-11} Torr equivalent nitrogen pressure.

According to Norton the permeability to helium is much lower for ceramics than for glass. This fact led Lafferty[13]

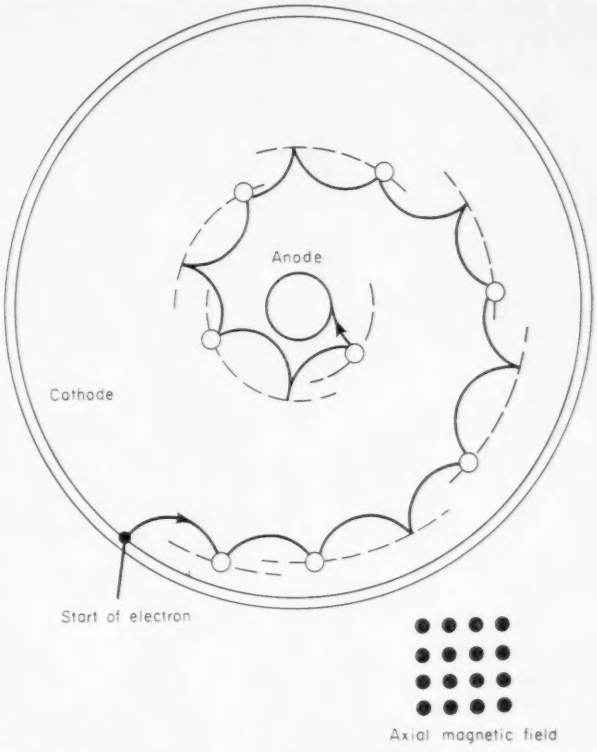


FIG. 9. Schematics of cold-cathode ionization gauge with symmetrical field. (R. Haefer[14]).

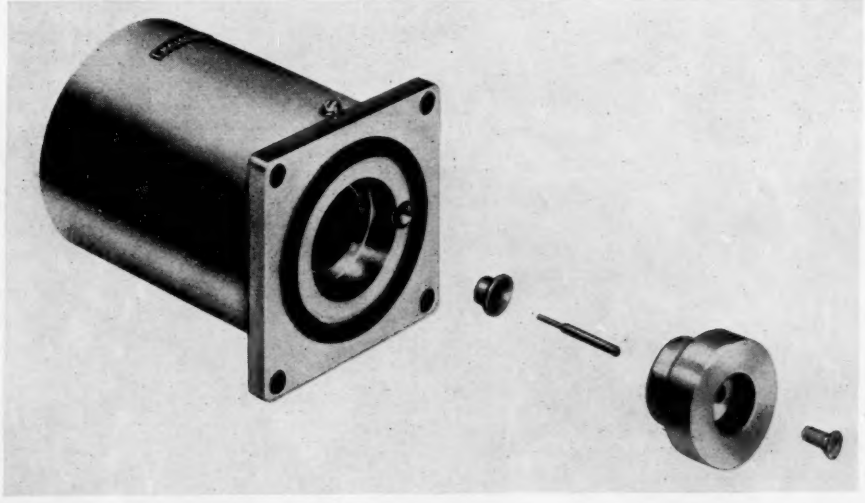


FIG. 10. Cold-cathode ionization gauge with symmetrical field ; photograph of disassembled tube ; inner pin is the anode (R. Haefer[14]).

to construct his ionization tube of fosterite ceramics. The influence of the vapor pressure of the filament material on the lower limit, calculated for tungsten at 2300°K, is about 10^{-12} Torr.

In technical vacuum equipment, the Penning type vacuum gauge is preferred since there is no hot filament to burn out. The earlier types normally did not have a uniform field since rings and even square-shaped electrodes were used. High fields always lead to unstable conditions because adsorbed molecules at edges can change emission processes. This, of course, resulted in stray currents of an uncontrollable nature which determined the lower limit, p_{min} was about 10^{-5} Torr. R. Haefer[14] built a more symmetrical electrode system (Figs. 9 and 10), which improved the lower limit by at least one order of magnitude.

P. A. Redhead[15], in a similar system, went even further by applying an auxiliary cathode for shielding the edges to prevent field emission from these edges. Redhead's gauge

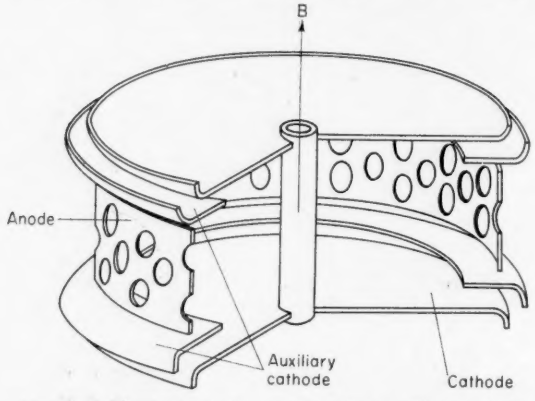


FIG. 11. Cold-cathode ionization gauge with auxiliary cathode for shielding field emission. (P. A. Redhead[15]).

(see Fig. 11) has led us into pressure regions so low that it is impossible for me to give any number for its defined lower limit.

Acknowledgements

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EXTRACT OF PANEL DISCUSSION CONCERNING THIS PAPER

Moderator : D. J. Santeler, General Electric, Schenectady, N.Y.

Panel Members : Dr. W. B. Nottingham, M.I.T., Cambridge, Mass.
Dr. P. A. Redhead, National Research Council, Ottawa, Canada.
Dr. Helmut Schwarz, Hamilton Standard Div. United Aircraft Corp., Windsor Locks, Conn.
Dr. G. Reich, E. Leybold's Nachfolger, Köln-Bayental, Germany.
Ivory Fish, Ratheon Co., Burlington, Mass.

Dr. Nottingham : Good accuracy can be obtained with the ion gauge and I feel as though the calibration that you obtain at higher pressures will hold right straight down to low pressure if you use good techniques.

Moderator : To put a number on this, is 10 per cent reasonable for good technique ?

Dr. Nottingham : I would say better than 10 per cent.

Moderator : Dr. Schwarz, how do you feel on this subject ?

Dr. Schwarz : I would say I agree with Dr. Nottingham's comments down to about 10^{-9} Torr, but not lower ; knowing very well the history of the gauge and what has been done with it before (baking out, kind of gas, etc.) a lower limit as defined in my paper is of the order of 10^{-9}. You cannot just use a gauge number X which Y had used and assume that Z will obtain the same accuracy for pressures lower than 10^{-8}–10^{-9} Torr without being sure whether Y and Z had done the same with it before.

Dr. Redhead : I would take issue with Dr. Schwarz on the question of the use of the mass spectrometer at low pressures. There is enough experimental evidence to show that the mass spectrometers capable of measuring partial pressures of 10^{-14} Torr can be constructed. My feeling is that once one is forced to work with a system pressure less than about 10^{-9} Torr, that a mass-spectrometer is the best instrument.

Moderator : What is the disadvantage or advantage of using a gauge with no glass envelope ?

Dr. Schwarz : In case we can disregard the impedance, there are two reasons for asking such a question, particularly, when we come down to pressures lower than 10^{-10} Torr ; in other words : when we work in a region where we have more molecules on the walls than in the volume, it is then more a two-dimensional problem rather than a three-dimensional one—(1) The wall might change the electrical field in the tube—(2) the wall is a place of continuous interchange of molecules between surface and volume. The two points are probably influencing each other ; secondary emission from surfaces depend on gas charge of these surfaces ; they change the surface charges and so on. It is then impossible to obtain a consistent calibration.

Dr. Nottingham : Let me disagree with that because I think that if you would design the gauge the way my gauge is designed and was described in 1954, the calibration is very accurately reproduced from gauge to gauge. We have made many calibrations and this is definitely a geometrical problem. You can have a good deal of confidence that my gauge may be calibrated in glass with its outside grid and if you use the same gauge in another environment without the glass being present, I would feel the calibration would be excellent.

Dr. Schwarz : I was talking about pressure ranges lower than 10^{-10}–10^{-11} Torr. I think that this is a different story.

Dr. Nottingham : Well, you are out of the Bayard–Alpert range anyway.

Dr. Schwarz : All my comments are not concerned with any specific ionization gauge but with ion gauges in general, at their lower limits claimed in some literature.

Moderator : Do you panelists have any questions that you would like to direct to each other as a final comment ?

Dr. Redhead : I would like to ask Dr. Schwarz a question. He made the point that in the Knudsen gauge one has to be sure that the accommodation coefficients on both the hot and cold surfaces must be the same. How can this be done in practice when one has to have a fairly large temperature difference between the two surfaces to get any sensitivity out of the gauge ? How, in practice, could one maintain equal accommodation coefficients ?

Dr. Schwarz : First of all, it is difficult to describe by what factors the accommodation coefficients are really determined. One of the most important factors are the conditions of surfaces as far as their gas and vapor adsorption layers are concerned. But we know that we can keep surfaces free from adsorbed gas or vapor molecules less than 10 per cent of a monolayer for quite some time—sufficient for calibration—if baked out under a vacuum lower than 10^{-9} Torr. Thus, it should be possible to obtain equal conditions of the two surfaces within the required accuracy.

This same problem we might have with the radiometer type gauge we have with the ion gauge, also ; but this is only one of the many other effects I pointed out in my paper that exists in the ion gauge and do not exist in the radiometer type gauge.

Moderator : I am afraid time is running out on us, so, I would like to thank this panel for their participation.

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Vacuum Sintering of Quartz Powder and Phase Transformation of Quartz

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The process of the phase transformation of quartz to silica glass in the range of heating time 10–120 min at the pressure of 10^{-5} Torr is as follows :

At the heating temperature below about 1700 °C
Quartz——→silica glass——→cristobalite;
At the heating temperature above about 1700 °C
Quartz——→silica glass.

Quartz transforms to silica glass from the surface of the quartz crystal. Since the surface of the material in general has no definite structure, the transformation temperature of quartz to silica glass ought to be considered not definite. The experiment using −60 mesh quartz powder indicated that sintering was produced by the surface tension of silica glass which appeared on the quartz surface. The silica glass concentration was over 25 per cent, and the heating temperature was above about 1600 °C. It is recognized that H_2O is discharged from quartz during the process of deformation of the quartz lattice by heat. H_2O content in the quartz used in this experiment was probably less than 0.1 per cent.

1. Introduction

Recently a great amount of transparent silica glass has been in demand for mercury bulbs and tubes, and tungsten lamps[1, 2].

As raw material for the transparent silica glass, quartz (mainly in powder form) is most popular, though quartz vein and silica gel (silicon halide) are also available[3].

Unfortunately, we have no accurate knowledge concerning the phase transformation process of quartz powder in the case of a moderately short heating period, and the amount of H_2O in quartz.

Three processes for making silica glass from quartz suggest themselves from Sosman's[4] phase diagram of silica at atmospheric pressure.

1. α quartz $\xrightarrow[573\,^\circ C]{}$ β quartz $\xrightarrow[867\,^\circ C]{}$ tridymite 1 $\xrightarrow[1470\,^\circ C]{}$ β cristobalite $\xrightarrow[1723\,^\circ C]{}$ silica glass.
2. α quartz $\xrightarrow[573\,^\circ C]{}$ β quartz $\xrightarrow[867\,^\circ C]{}$ tridymite 1 $\xrightarrow[1680\,^\circ C]{}$ silica glass.
3. α quartz $\xrightarrow[573\,^\circ C]{}$ β quartz $\xrightarrow[?]{}$ silica glass.

In these processes, the following transformations are sluggish :

β quartz $\rightleftharpoons$ tridymite 1
tridymite 1 $\rightleftharpoons$ β cristobalite
β cristobalite $\rightleftharpoons$ silica glass.

During the industrial process of producing silica glass, quartz is heated up to some required temperature to produce silica glass in a short period of time.

Therefore, among the above three processes, the third process is the most probable to occur. It was confirmed by Roberts[5] in 1959 and by Chaklader and Roberts[6] in 1961 that the transformation of quartz to cristobalite was indirect and involved a transitional, noncrystalline phase for a heating range of 1270–1650 °C at atmospheric pressure. The transformation is as follows :

Quartz——→transitional phase——→cristobalite.

This process may be considered as a mixed process of both the third and the reverse of the first process explained above. However, it was recently reported and discussed by Mackenzie[7] that the following processes of the quartz–cristobalite transformation are equally possible and are sensitive to the ambient atmosphere :

Quartz——→liquid——→cristobalite. (1)

Quartz——→cristobalite. (2)

Mackenzie states that the melting point of quartz is definitively below 1450 °C and possibly above 1400 °C.

Concerning the sintering of the quartz powder, it was reported by Chaklader and Roberts[8] in 1959 that a noncrystalline phase which appears on quartz during heating in air is responsible for sintering. The object of this experiment is to determine the phase transformation of quartz to silica glass, to observe the sintering of quartz powder, and to measure the weight loss of quartz and the infra-red absorption

at about 3μ in the samples of melted silica glass and to relate these effects to the water content. Several grain sizes of quartz powder were used, and the experiments conducted in the range of heating temperature 1460–1745 °C and heating time 10–120 min at the pressure of 10^{-5} Torr.

2. Experimental

2.1. *Vacuum furnace*

The heater and the reflector of the vacuum furnace (Fig. 1)

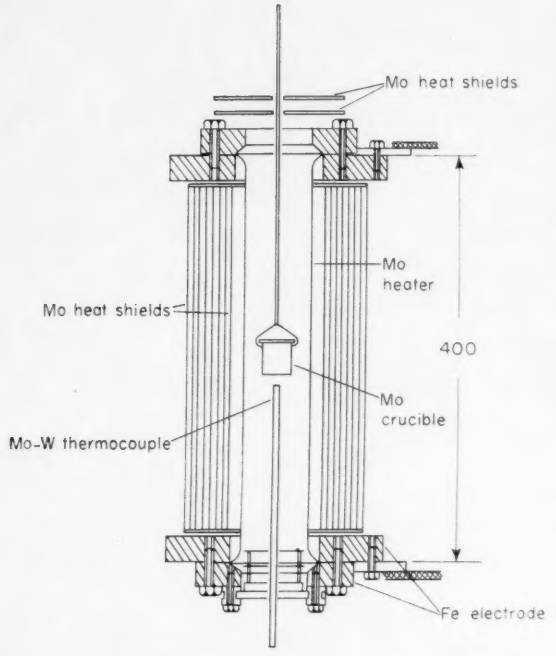

FIG. 1. Vacuum furnace.

used for the experiment of the phase transformation of quartz and the sintering of the quartz powder were constructed mainly of 0.1 mm thick molybdenum plate in order to maintain a pressure of 10^{-5} Torr during heating. The heater consisted of three strips of molybdenum arranged to shape a cylinder, 400 mm in length and 65 mm in diameter. Temperature was attained by resistance heating. Vacuum was obtained by means of an oil diffusion pump having a speed of 4000 l/sec. The temperature of a crucible was measured by a Mo-W thermocouple[9] placed 5 mm below the crucible. The Mo-W thermocouple was calibrated against another Mo-W thermocouple inserted into the quartz powder in the crucible.

2.2. *Quartz powder*

In this experiment, −60 mesh powder, whose grain size distribution is shown in Table I for a typical sample, was mainly used.

In addition, −100, −200 and −325 mesh powders were also tested. These were prepared by means of screening −60 mesh powder with 100, 200 and 325 mesh sieves, respectively.

The −60 mesh powder micrograph is shown in Fig. 2.

FIG. 2. Micrograph of −60 mesh quartz powder. ×100.

TABLE I

Example of −60 mesh powder grain size distribution

Grain size mesh	Fraction (%)
−60– +100	60.2
−100– +150	28.3
−150– +200	5.7
−200– +250	3.3
−250– +325	1.4
−325– +400	0.4
−400–	0.2
Screening loss	0.5

2.3. *Procedures*

2.3.1. *Phase transformation determination and sintering state observation.* The crucible used in these experiments (Fig. 3) was cleaned by heating it for 60 min at 1760 °C at a pressure of 10^{-5} Torr, and then charged loosely with 20 g of quartz powder (−60, −100, −200, −325 mesh).

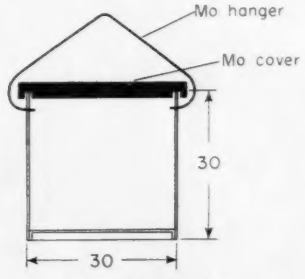

FIG. 3. Mo crucible.

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The crucible was inserted into the heater maintained at the temperature of 250°C, and the temperature then raised up to the desired experimental heating temperature within 20 min, and maintained constant at that temperature for the definite period of time at a pressure of 10^{-5} Torr.

After heating, the crucible was pulled out from the heater and cooled in vacuum.

The range of heating temperature was 1460–1745°C and the heating times were 10, 20, 40, 60 and 120 min. Separate samples were prepared for each of the heating temperatures and the heating times mentioned above.

The determination of the phase transformation of quartz to silica glass was performed by means of X-ray analysis of the test sample.

The sintering states were determined by observing the states of the quartz powder in the crucible and by observing thin sections of the sintered block of the test sample with a polarized microscope, and by measuring the change of the top level of the quartz powder in the crucible (nearly proportional to the volume change of quartz powder in the crucible) with the apparatus shown in Fig. 4.

2.3.2. *Weight loss measurement of quartz powder during heating.* Measurement of weight loss of quartz powder during heating was accomplished by measuring the weight of quartz powder in a Pt/Rh (Rh 40 per cent) crucible before and after heating for each test sample which was prepared for the definite heating temperature and heating time. As a Pt/Rh (Rh 40 per cent) crucible has a measurable weight loss in the temperature range of 1460–1745°C, continuous weighing is impossible.

2.3.3. *Infra-red absorption measurements.* Infra-red absorption spectra of the translucent or transparent samples, produced in these experiments, as well as those of crystalline quartz and oxyhydrogen-flame-fused silica glass were measured in the 2.5–5μ region.

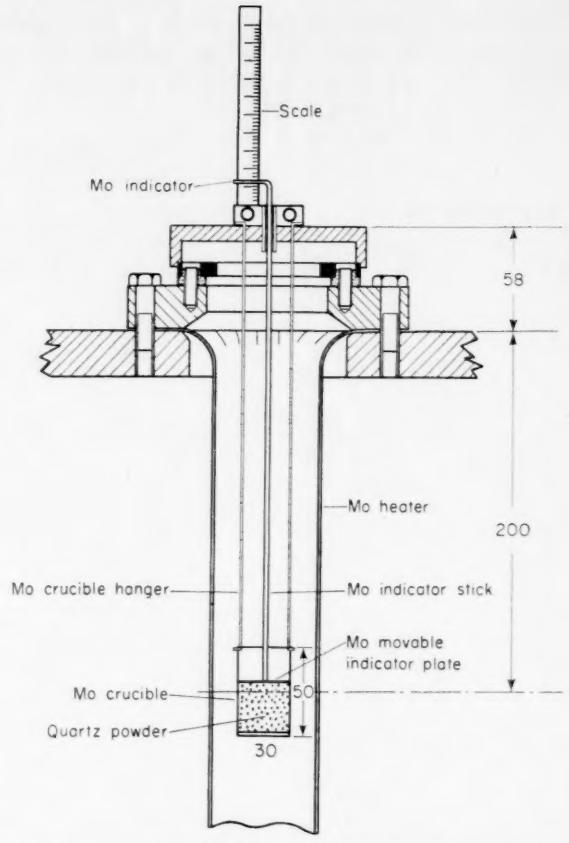

FIG. 4. Apparatus for measuring the volume change of quartz powder in crucible during heating.

3. Results

3.1. *Phase transformation of quartz*

The concentrations of quartz, cristobalite and silica glass made by heating −60 mesh quartz powder in Mo crucibles at various temperatures for 10 min were analysed by X-ray diffraction as shown in Fig. 5, and also in Fig. 6, for 60 min heating and in Fig. 7 for 120 min heating.

Tridymite could not be recognized by X-ray analysis in any test sample, nor cristobalite in case of 10 min heating, but the latter was recognized in cases of 60 min and 120 min heating.

It is evident from Fig. 5, that silica glass, not cristobalite, appears on the quartz surface at the first stage of heating.

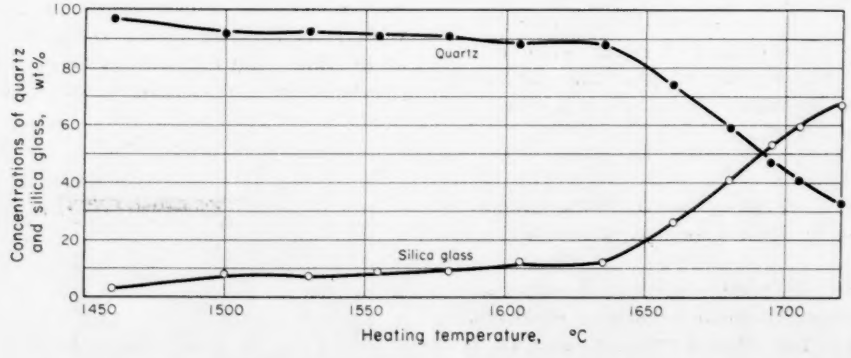

FIG. 5. Concentrations of quartz and silica glass after 10 min heating of −60 mesh quartz powder at various heating temperatures.

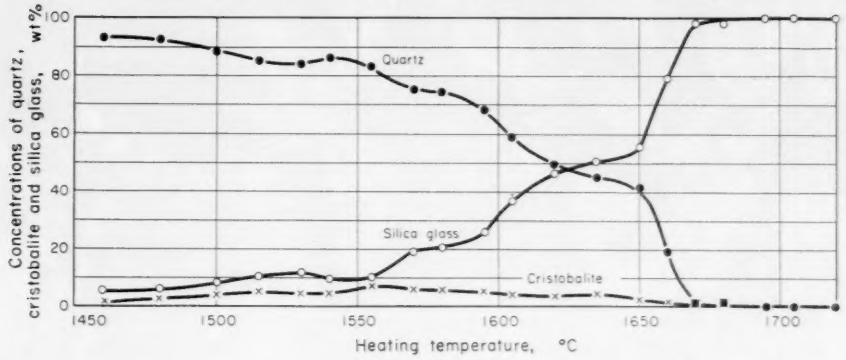

FIG. 6. Concentrations of quartz, cristobalite and silica glass after 60 min heating of −60 mesh quartz powder at various heating temperatures.

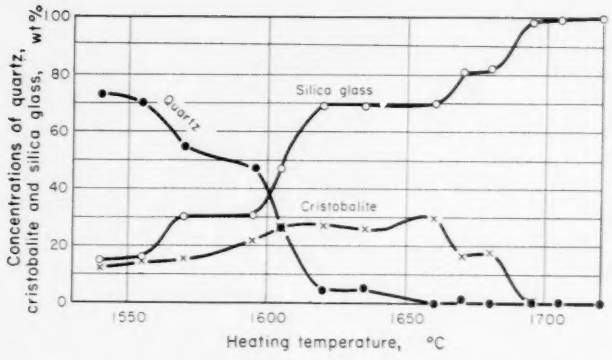

FIG. 7. Concentrations of quartz, cristobalite and silica glass after 120 min heating of −60 mesh quartz powder at various heating temperatures.

Comparing the concentrations of quartz, cristobalite, and silica glass on heating of quartz powder for the cases of 60 and 120 min at 1660°C, the percentage of quartz is changed from 19 to 0, that of cristobalite from 2 to 30, and that of silica glass from 79 to 70.

It is obvious, therefore, that cristobalite is transformed not from quartz directly but from silica glass.

The phase transformation of quartz vs. heating time at 1705°C is presented in Table II. Particularly, it is noticeable that cristobalite has not appeared in any test sample at any heating time.

TABLE II

Concentrations of quartz, cristobalite, and silica glass vs. heating time at 1705°C for −60 mesh quartz powder

Heating time (min)	Quartz (%)	Cristobalite (%)	Silica glass (%)
10	41	0	59
20	3	0	97
40	0	0	100
60	0	0	100
120	0	0	100

The grain size effect in the phase transformation of quartz is shown in Tables III and IV.

TABLE III

Concentrations of quartz, cristobalite and silica glass vs. the grain size of quartz powder for 60 min heating at 1660°C

Grain size of quartz powder mesh	Quartz (%)	Cristobalite (%)	Silica glass (%)
−60	23	4	73
−100	8	8	84
−200	0	25	75
−325	0	36	64

TABLE IV

Concentrations of quartz, cristobalite and silica glass vs. the grain size of quartz powder for 10 min heating at 1705°C

Grain size of quartz powder mesh	Quartz (%)	Cristobalite (%)	Silica glass (%)
−60	41	0	59
−100	33	0	67
−200	30	0	70
−325	0	0	100

The smaller the grain size of the quartz powder, the larger the rate of transformation.

3.2. *State of sintering quartz powder by heating*

Fig. 8 presents several photographs of the transformed state of quartz powder (−60 mesh) in the crucible which was heated at the indicated temperatures, and the several micrographs of the thin sections of the heated matter in the crucible under the cross-polarized light.

Quartz powder does not sinter observably after 60 min of heating at 1500°C as in Fig. 8(a-1), but powder grains begin to bind each other at 1580°C, and the volume of the quartz powder in the crucible swells as in Fig. 8(b-1).

As shown in Fig. 8(b-2), the micrographic observation revealed that the optically insensitive layer containing a little optically sensitive cristobalite patterns was appearing on the grain surface and producing bonds between grains. Also the optically sensitive cristobalite patterns were found on the grain surface as shown in the micrograph of Fig. 8(b-3).

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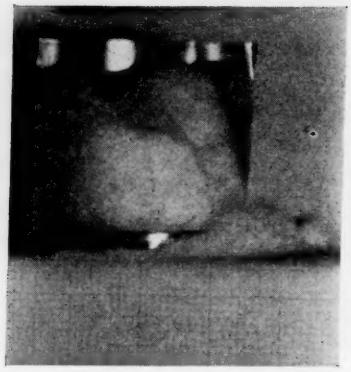
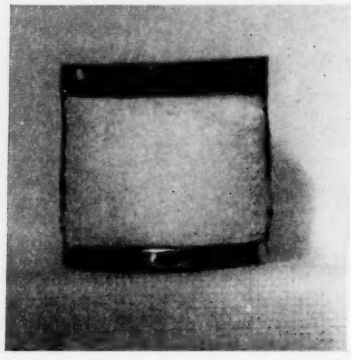


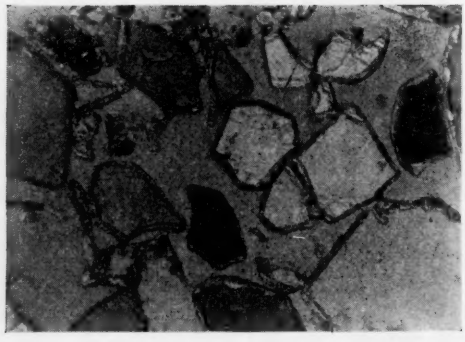
8(a-1). Quartz powder is slightly agglomerated in crucible. ×1.

8(a-2). Micrograph of thin section under cross-polarized light of slightly agglomerated quartz powder. ×100.

FIG. 8(a). State of quartz powder in Mo crucible after 60 min heating at 1500°C.



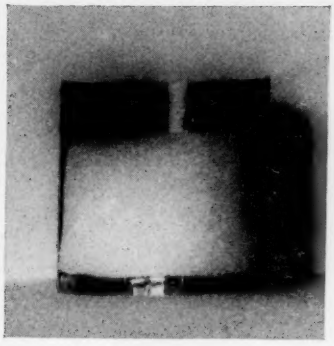
8(b-1). Volume of quartz powder is swelled slightly in crucible. ×1.



8(b-2). Micrograph of thin section of slightly swelled quartz powder shown in 8(b-1). Optically insensitive layer having a little optically sensitive cristobalite patterns can be seen on the crystal grains under cross-polarized light. ×100.

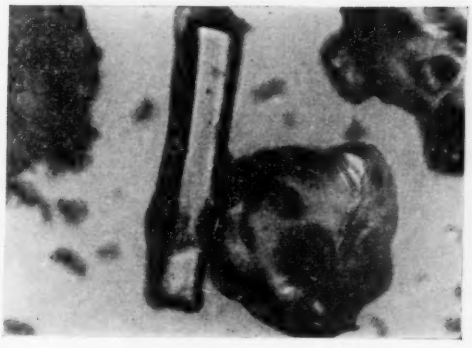
8(b-3). Optically sensitive cristobalite patterns on the crystal grain surface. ×100.

FIG. 8(b). State of quartz powder in Mo crucible after 60 min heating at 1580°C.



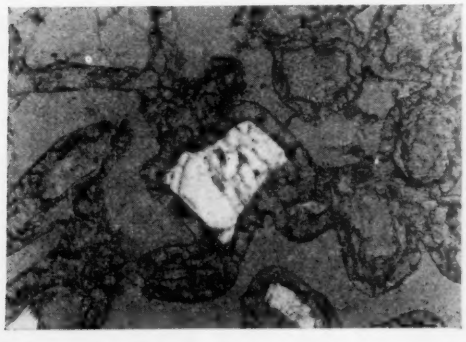
8(c-1). Quartz powder is sintered in crucible. ×1.

8(c-2). Micrograph of thin section of sintered quartz powder shown in 8(c-1) under cross-polarized light. ×100.



8(c-3). Showing lens formation between the crystal grains. ×100.

FIG. 8(c). State of quartz powder in Mo crucible after 60 min heating at 1605°C.



8(c′-1). Micrograph of thin section of sintered quartz powder heated at 1605°C for 120 min under cross-polarized light. Optically sensitive cristobalite patterns are seen in the optically insensitive layer on the crystal grain. ×100.

FIG. 8(c′). State of quartz powder in Mo crucible after 120 min heating at 1605°C.

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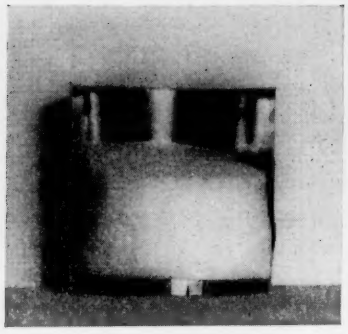
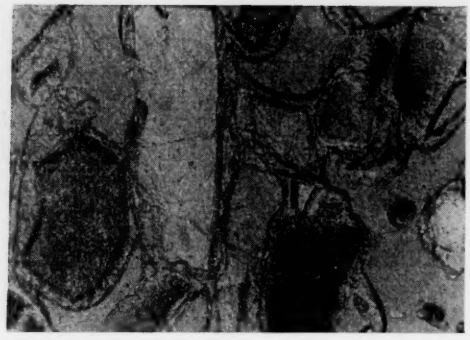
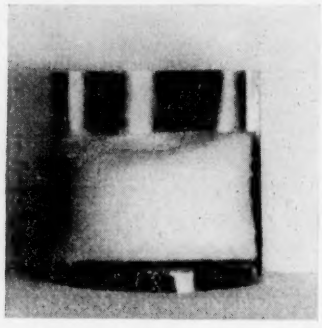


8(d-1). Quartz powder is sintered in crucible. ×1.

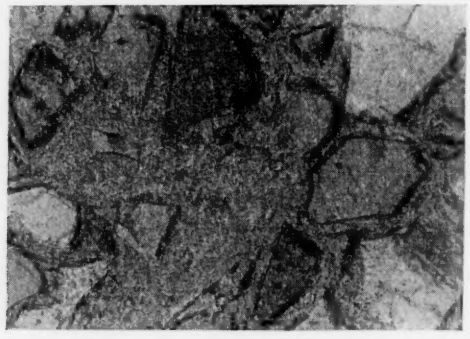


8(d-2). Micrograph of thin section of sintered quartz powder shown in 8(d-1) under cross-polarized light. Optically insensitive layers become thicker. ×100.

FIG. 8(d). State of quartz powder in Mo crucible after 60 min heating at 1620°C.

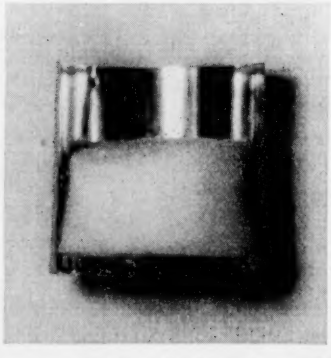


8(e-1). Quartz powder is sintered in crucible. ×1.



8(e-2). Micrograph of thin section of sintered quartz powder shown in 8(e-1) under cross-polarized light. ×100.

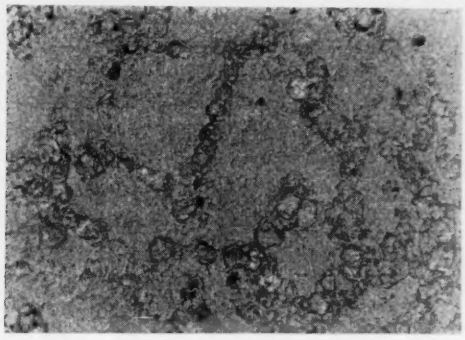
FIG. 8(e). State of quartz powder in Mo crucible after 60 min heating at 1635°C.



8(f-1). Quartz powder is heavily sintered in crucible. ×1.

8(f-2). Micrograph of thin section of sintered quartz powder shown in 8(f-1) under cross-polarized light. Quartz crystals are floating in the optically insensitive field. Optically sensitive cristobalite patterns can be seen slightly at the initial position of the boundary of crystal grain. ×100.

FIG. 8(f). State of quartz powder in Mo crucible after 60 min heating at 1660°C.



8(f′-1). Micrograph of thin section of sintered quartz powder heated at 1660 °C for 10 min under cross-polarized light. Optically sensitive cristobalite patterns have appeared where the boundary of crystal grain had existed. ×100.

FIG. 8(f′). State of quartz powder in Mo crucible after 120 min heating at 1660 °C.

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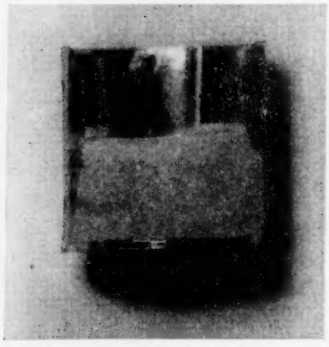
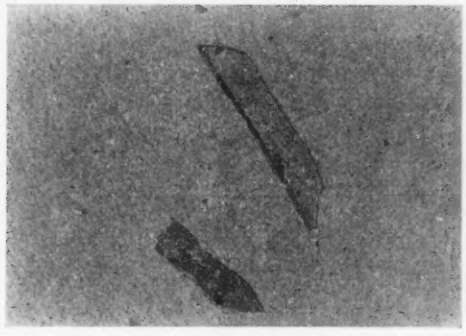
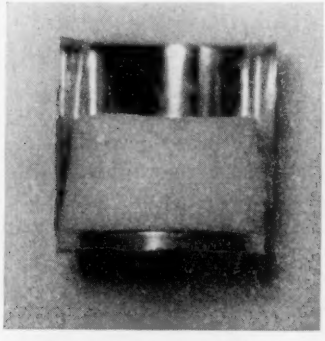


8(g-1). Sintered block became translucent. ×1.



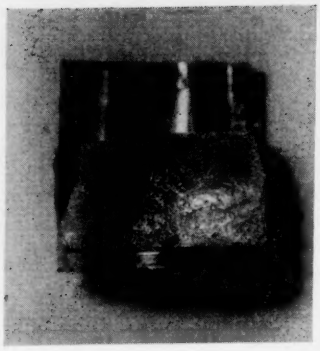
8(g-2). Micrograph of thin section of translucent block shown in 8(g-1) under cross-polarized light. ×100.

FIG. 8(g). State of quartz powder in Mo crucible after 60 min heating at 1670 °C.



8(g′-1). After 120 min heating at 1670 °C the translucent block became again opaque. ×1.

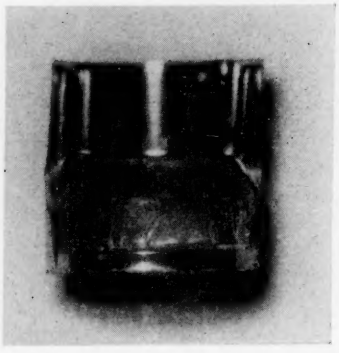
FIG. 8(g′). State of quartz powder in Mo crucible after 120 min heating at 1670 °C.



8(h-1). Transparent block appeared in crucible. ×1.

8(h-2). Micrograph of thin section of transparent block shown in 8(h-1) under cross-polarized light. ×100.

FIG. 8(h). State of quartz powder in Mo crucible after 60 min heating at 1695°C.



8(i-1). Blackish silica glass block in crucible. ×1.

8(i-2). Micrograph of thin section of blackish silica glass shown in 8(i-1) under cross-polarized light. Mo and Mo oxides deposits can be seen like a net. ×100.

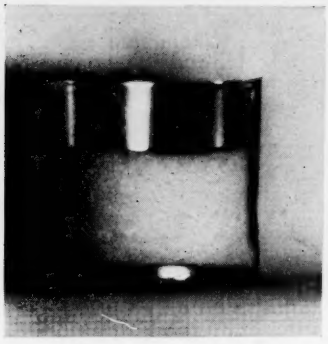
FIG. 8(i). State of quartz powder in Mo crucible after 60 min heating at 1745°C.

Sintering was actually recognized on heating at 1605°C. Figs. 8(c-2) and 8(c-3) illustrate that the grains are being attracted mutually by flow of optically insensitive layers. After 120 min heating, the optically sensitive cristobalite patterns are observed very distinctly on the grain boundary as in Fig. 8(c′-1).

As the temperature is raised up to 1620, 1635 and 1660°C, sintering continues, and voids disappear as in Figs. 8(d-1), 8(d-2) 8(e-1), 8(e-2), 8(f-1) and 8(f-2), and finally at 1660°C crystal grains become smaller and begin to float in the optically insensitive field. At the end of 120 min heating at 1660°C, however, grains disappear, and the optically sensitive cristobalite patterns appear instead in the place where grain boundaries are considered to have existed as in Fig. 8(f′-1).

A translucent block is obtained after 60 min heating at 1670°C, as in Figs. 8(g-1) and 8(g-2), but after 120 min heating, the translucent block becomes opaque as shown in Fig. 8(g′-1).

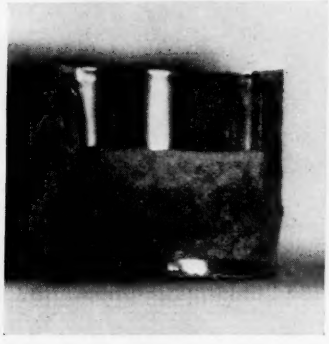
Quartz powder is transformed to the transparent block in 60 min heating at 1695°C as shown in Figs. 8(h-1) and 8(h-2), but it becomes blackish in the case of the heating temperature of 1745°C as in Fig. 8(i-1). A sort of net-shaped material is observed in the thin section of this material as in Fig. 8(i-2).



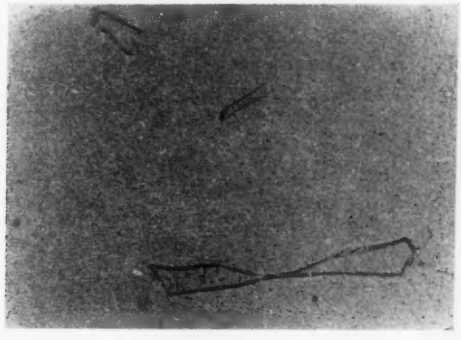
9(a-1). Quartz powder is sintered in crucible. ×1.

9(a-2). Micrograph of thin section of sintered quartz powder shown in 9(a-1) under cross-polarized light. ×100.

FIG. 9(a). State of quartz powder in Mo crucible after 10 min heating at 1705°C.

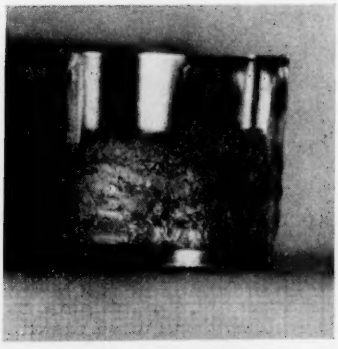


9(b-1). Quartz powder becomes translucent block in crucible. ×1.

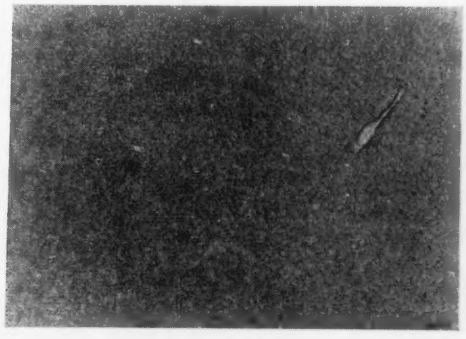


9(b-2). Micrograph of thin section of translucent block shown in 9(b-1) under cross-polarized light. ×100.

FIG. 9(b). State of quartz powder in Mo crucible after 20 min heating at 1705°C.



9(c-1). Quartz powder becomes transparent block in crucible. ×1.



9(c-2). Micrograph of thin section of transparent block shown in 9(c-1) under cross-polarized light. ×100.

FIG. 9(c). State of quartz powder in Mo crucible after 40 min heating at 1705°C.

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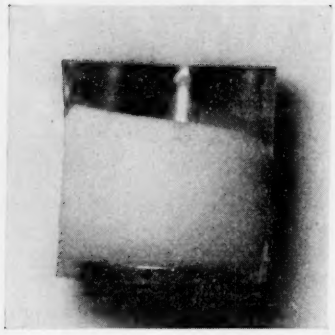
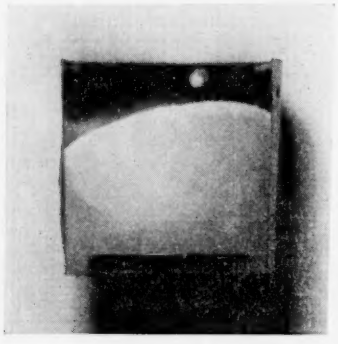


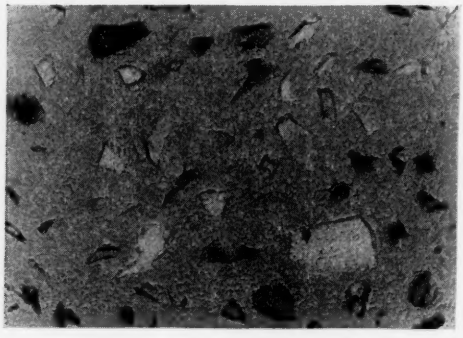
10(a-1). Quartz powder is heavily sintered in crucible. ×1.

10(a-2). Micrograph of thin section of sintered quartz powder shown in 10(a-1) under cross-polarized light. ×100.

FIG. 10(a). State of quartz powder in Mo crucible after 10 min heating of −100 mesh quartz powder at 1705 °C.

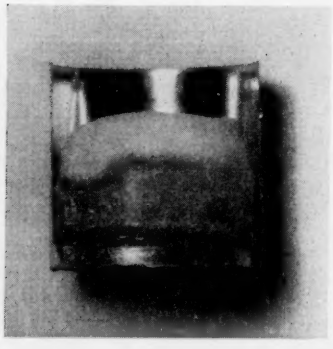


10(b-1). −200 mesh quartz powder becomes partly semitranslucent in crucible. ×1.

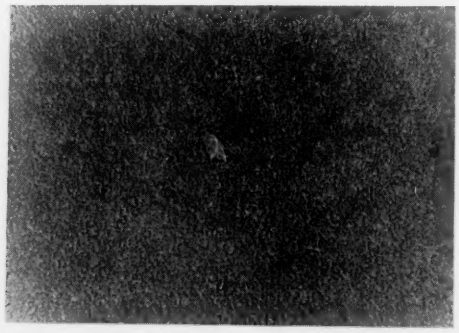


10(b-2). Micrograph of thin section of sintered quartz powder shown in 10(b-1) under cross-polarized light. ×100.

FIG. 10(b). After 10 min heating of −200 mesh quartz powder at 1705 °C.



10(c-1). Quartz powder becomes partly transparent block in crucible. ×1.



10(c-2). Micrograph of thin section of semitransparent block shown in 10(c-1) under cross-polarized light. ×100.

FIG. 10(c). After 10 min heating of −325 mesh quartz powder at 1705 °C.

It was determined qualitatively that the origin of this blackening was a mixture of Mo and Mo oxide. Fig. 9 shows the state of sintering vs. heating time. A transparent block is obtained in 40 min heating at 1705°C. Fig. 10 shows that the smaller the grain size of the quartz powder used, the higher is the rate of sintering.

3.3. *Infra-red absorption spectra of silica glass*

Infra-red absorption spectra of a crystalline quartz, oxyhydrogen-flame-fused silica glass, and a vacuum-melted silica glass of 1 mm thick plates were measured in the 2.5–5μ region (Fig. 11). The vacuum-melted silica glass has no absorption at about 3μ.

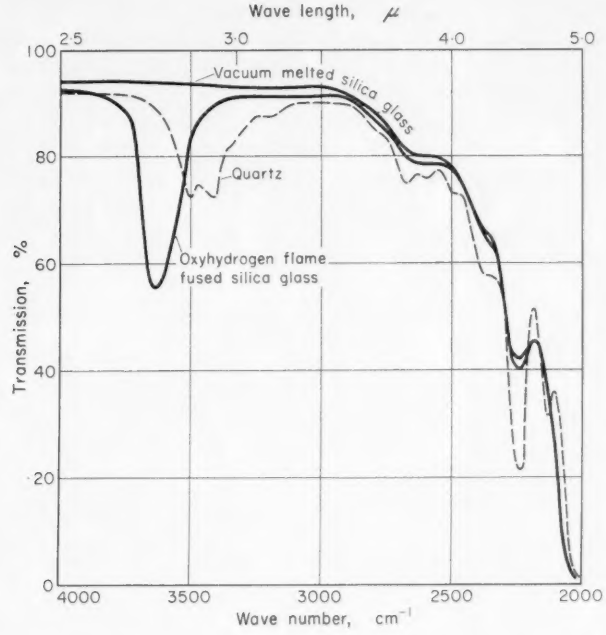


FIG. 11. Transmission curves for quartz, oxyhydrogen flame fused silica glass and vacuum melted silica glass 1 mm thick.

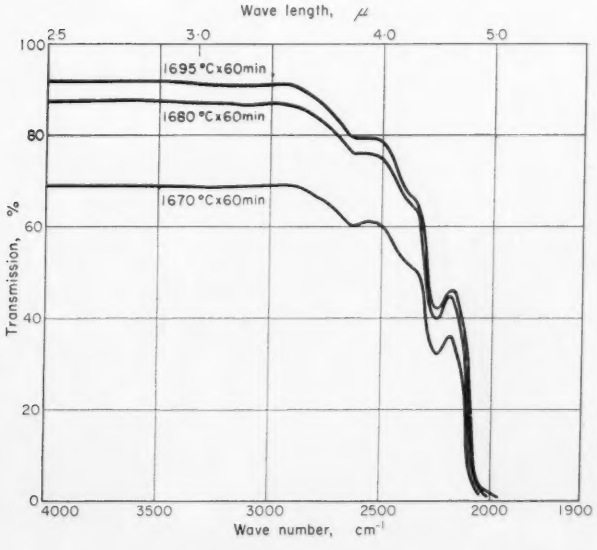


FIG. 12. Transmission curves for vacuum melted silica glass, 1670°C × 60 min heating, 1680°C × 60 min heating and 1695°C × 60 min heating.

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Fig. 12 shows the absorption spectra of 1 mm thick plates of the test samples which were made by heating the quartz powder at 1670, 1680 and 1695°C for 60 min respectively. They have no absorption at about 3μ. In the cases of the vacuum-melted, thicker plate, however, weak absorption was observed at 3.1–3.2μ as shown in Fig. 13.

3.4. *Volume change of quartz powder in crucible during heating*

Fig. 14 illustrates the effect of the heating temperature on the displacement of the indicator plate which was placed on the quartz powder in the crucible in the apparatus shown in Fig. 4.

As a general tendency, the volume of quartz powder slightly shrinks initially and in the next stage swells a little with the increase of temperature.

For heating below about 1600°C, the volume of quartz powder does not shrink, but when the temperature is above about 1600°C sintering does occur. These tendencies confirm the results shown in Fig. 8.

3.5. *Weight-loss of quartz during heating*

The percentages of the weight-loss of quartz and of the transformation from quartz during heating at various temperatures for 60 min and 120 min are plotted in Figs. 15 and 16. Curves of weight-loss and transformation are very similar in shape up to about 90 per cent transformation. Evaporation of SiO_2 from quartz, however, increases rapidly above about 1700°C, and the weight-loss becomes very much larger. Weight-loss percentages against transformation percentages are nearly equal for both 60 min and 120 min heatings. Weight-loss caused by constituents other than SiO_2 could not be measured or analysed, except

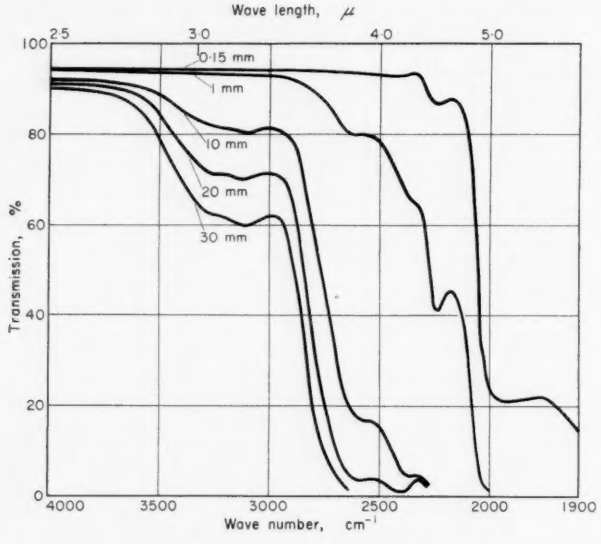

FIG. 13. Transmission curves for vacuum melted silica glass with 0.15 mm, 1 mm, 10 mm, 20 mm and 30 mm thick.

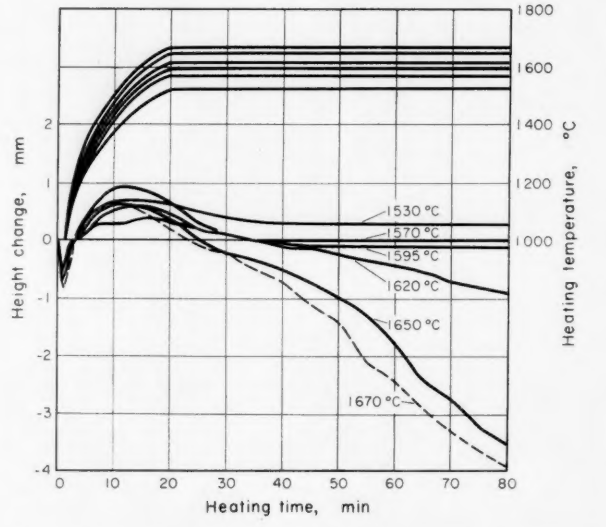

FIG. 14. Effects of heating temperature and heating time on the change of the top level of quartz powder in crucible.

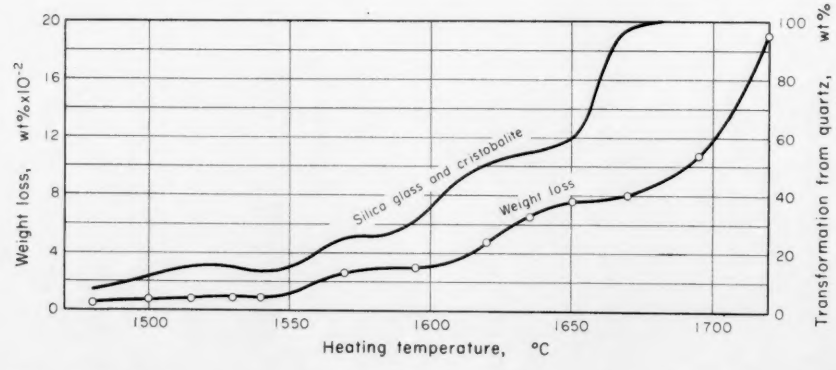

FIG. 15. Weight-loss of quartz powder and transformation from quartz after 60 min heating at various heating temperatures.

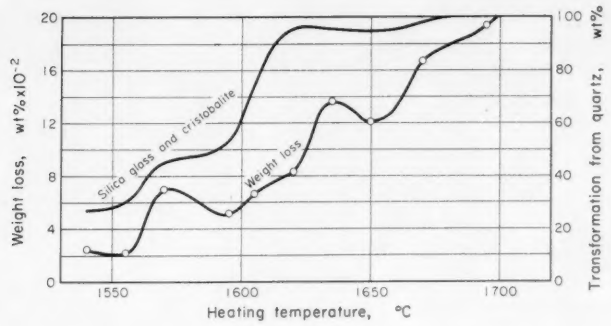

FIG. 16. Weight-loss of quartz powder and transformation from quartz after 120 min heating at various heating temperatures.

that weight-losses at 90 per cent transformation were about 8×10^{-2} per cent in both cases.

As it is hard to believe that there is a heavy evaporation of SiO_2 at the temperature of 90 per cent transformation, the greater part of 8×10^{-2} per cent weight-loss at 90 per cent transformation is assumed to be caused by impurities in quartz.

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4. Discussion

4.1. *Phase transformation of quartz*

On heating quartz powder in vacuum in the range of 10–120 min heating time and 1460–1745 °C heating temperature, quartz did not convert to tridymite. Recently, Holmquist[10] found that tridymite is pictured as a binary incongruently melting phase containing a small amount of metal oxide.

It is recognized as the result of the X-ray analysis that the optically insensitive layer on the surface of quartz, which is demonstrated by the micrographs in Figs. 8(b-2), 8(c-2) and 8(d-2), is silica glass. Therefore, the transformation of quartz is considered to start at the surface of quartz[11].

As the surface of the material generally has no definite structure, it may be assumed that the transformation temperature of quartz to silica glass is not constant.

In the classification of the phases of quartz at atmospheric pressure reported by Sosman, the transformation temperature of quartz to silica glass is indicated by the mark " ? ". The transformation temperature, however, ought to be considered indefinite, rather than just " ? ". This consideration on the transformation temperature of quartz is also different from Mackenzie's.

From the results of X-ray analysis as presented in Figs. 5, 6 and 7, it is believed that cristobalite converts not directly from quartz but from silica glass.

Hence, the process of the transformation of quartz at the temperature below about 1700 °C is expressed as follows :

Quartz⟶silica glass⟶cristobalite.

A similar relation is reported by Roberts[5], and Chaklader and Roberts[6]. When the heating temperature is above about 1700 °C, however, the silica glass does not convert to cristobalite, i.e. the following process occurs in the transformation of quartz :

Quartz⟶silica glass.

As the finer-grain powder has a larger surface area for equal weight of quartz powder, the quartz transforms to silica glass more easily when finer grain is used.

4.2. *Sintering of quartz powder*

From the result of the volumetric change experiment and the result of the sintering experiment, it is apparent that the sintering occurs above about 1600 °C and, on the contrary, the volume swelling occurs below about 1600 °C. At the heating temperature of 1600 °C for 60 min, the amount of densification of silica glass in powder form becomes about 25 per cent, and grains of powder are attracted to each other by the silica glass layer which is able to flow.

It should not be difficult to understand that the surface tension of silica glass is a motive force for sintering of quartz powder. Therefore, if each of the grains were able to move as freely as possible, quartz powder would be more easily sintered.

4.3. H_2O *in quartz*

Vacuum-melted silica glass has less absorption in the range 2.5–4μ as compared with the crystalling quartz and the oxyhydrogen-flame-fused silica glass as shown in Fig. 11.

It may thus be assumed that H_2O, OH ions and OH groups are not contained in the vacuum-melted silica glass[12, 13].

In the experiment on sintering in a Mo crucible at above about 1700 °C, Mo and Mo oxide, which were produced by the following reaction, are dispersed into quartz powder before completion of sintering :

$$Mo + 2H_2O \rightleftharpoons MoO_2 + 2H_2. \quad (1)$$

Then they are fixed in the quartz powder after sintering.

Such net-like deposit as shown in Fig. 8(i-2) indicates distinctly that Mo and Mo oxide were deposited on the surface of quartz grain before sintering. In short, this phenomenon shows that H_2O has been discharged from quartz during heating.

As the weight loss experiment shows that the weight loss percentages of quartz are proportional to the quartz transformation percentages, it should be agreed that H_2O and

other impurities have been discharged from the quartz when the lattice structure of the quartz is deformed by heating.

The weight loss percentage at 90 per cent transformation is about 0.1 in both 60 and 120 min heating. Hence, H_2O content in quartz is believed to be less than 0.1 per cent.

Acknowledgements

The author wishes to express his sincere thanks to Dr. T. Harada for his interest and encouragement, and to Mr. K. Asano for his assistance during the experiments. In addition, he wishes to thank Mr. Y. Fukao and Mr. Y. Hayasi for their X-ray analysis, Mr. G. Imotani, Dr. T. Takamura, and Mr. T. Kubota for many valuable discussions on the infra-red absorption of silica, and Mr. S. Niwa for his chemical analysis of Mo in silica glass. The support of this research by Toshiba Denko Co., Ltd., is gratefully acknowledged.

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Conference

The Institute of Physics and The Physical Society

THE INSTITUTE OF PHYSICS AND THE PHYSICAL SOCIETY has announced that a one day symposium on " Some aspects of vacuum science and technology " will be held at Imperial College of Science and Technology, London, on 5 January 1962.

The scope of the symposium will be : (a) continuously exhausted bakable vacuum apparatus for pressures below 10^{-9} mm of mercury ; and (b) the controlled deposition of evaporated film.

It is stated that further details and application forms will be available about the end of October, 1961, from the Administration Assistant, The Institute of Physics and The Physical Society, 47 Belgrave Square, London, S.W.1.

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Book Review

VACUUM TECHNOLOGY TRANSACTIONS, Proceedings of the Seventh National Symposium. Edited by C. R. Meissner. Pergamon Press, Oxford, 1961, pp. 427, £7 7s.

THIS VOLUME contains the papers presented at Cleveland, Ohio in October 1960 at the seventh symposium arranged by the American Vacuum Society. Over 70 papers are included on a wide range of topics, and it is impossible to review them in detail here. A general impression of the attention given to the principal aspects of vacuum technology can, however, be gained from the following list of the numbers of papers devoted to them. Pumping systems, 15 ; components, 7 ; systems, 7 ; pressure measurements, 10, with an additional 7 papers on partial-pressure measurements ; industrial applications, 10, with a further 15 papers on thin films. Although several of the papers originated in Europe, Australia, Canada and Japan, the vast majority are, of course, by authors from the U.S.A. The striking activity of American industrial organizations in the field is demonstrated by the fact that over half of the papers came from this source.

Although a few novel developments are described, most of the papers deal with advances in the well-established fields of vacuum technology. There are a few surprising omissions from the material covered, for example there is no discussion of cryogenic pumping systems. New applications of vacuum techniques to space research were discussed by Dr. Abbott of N.A.S.A. during the symposium, but his lecture is not reproduced in the Proceedings.

The standard of reproduction of the volume is excellent, and the publishers are to be congratulated on preparing it so soon after the conference. It is, however, to be regretted that no account is included of the discussion following the presentation of the papers. Everyone interested in vacuum technology will wish to see the volume, but its cost is so high that they may need to do so in libraries.

D. W. HOLDER

Organisation internationale pour la Science et la Technique du Vide

International Organization for Vacuum Science and Technology

Internationale Organisation für Vakuum-Physik und -Technik

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EDITORIAL — LEITARTIKEL

Des sociétés nationales du vide se sont créées récemment ou sont en voie de formation. Il est certain qu'elles contribueront dans une large mesure au développement des sciences et techniques du vide.

Nous sommes également heureux d'annoncer que l'étude de la transformation de l'OISTV en une fédération comprenant aussi les spécialistes des pays où n'existent pas de sociétés nationales se poursuit et que cette transformation pourrait être réalisée au cours des prochains mois.

*
* *

Vacuum national bodies have been recently set up or are being constituted. They will doubtless bring a large contribution to the development of vacuum science and technology.

We are equally pleased to announce that the study of the evolution of the IOVST towards a federation which would also group the specialists from countries where national bodies do not exist, is being pursued and that this evolution could be realized within the next few months.

*
* *

Nationale Vakuum-Gruppen haben sich kürzlich gebildet oder sind im Entstehen. Es besteht kein Zweifel, dass sie in grossem Masse zur Entwicklung der Vakuum-Physik und -Technik beitragen.

Ausserdem freut es uns mitteilen zu können, dass die Studien über eine Umformung der IOVPT in eine Organisation, der auch die Spezialisten der Länder angehören werden, in denen noch keine nationalen Gruppen bestehen, fortgeführt werden. Diese Umformung dürfte im Laufe der nächsten Monate abgeschlossen sein.

*
* *

1. 2e Congrès International de la Science et de la Technique du Vide (1961)

2nd International Congress on Vacuum Science and Technology (1961)

2. Internationaler Kongress für Vakuum-Physik und -Technik (1961)

Rappelons que ce congrès organisé par l'American Vacuum Society (AVS) et patronné par l'OISTV se tiendra au Sheraton-Park Hotel à Washington, D.C. (U.S.A.), du 16 au 19 octobre 1961. A cette occasion auront lieu l'Assemblée Générale Statutaire de l'OISTV et une exposition internationale de matériel de vide.

On peut prévoir dès à présent que le congrès et l'exposition remporteront un très grand succès.

Notre Secrétariat a envoyé aux membres de l'OISTV ne résidant pas aux Etats-Unis d'Amérique divers documents relatifs au congrès (bulletin d'adhésion, avant-programme, liste d'hôtels, carte de réservation d'hôtel). Ces documents ont été envoyés par l'AVS à nos membres résidant aux Etats-Unis.

Ceux de nos membres désireux d'assister au congrès sont priés de s'inscrire sans tarder, s'ils ne l'ont pas encore fait.

Les comptes rendus du congrès seront publiés par Pergamon Press en deux volumes comprenant au total plus de 1000 pages, et dont le prix est de $35.00 *en cas de commande lors du congrés.*

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We recall that this congress organized by the American Vacuum Society (AVS) and sponsored by the IOVST will be held at the Sheraton-Park Hotel, Washington, D.C. (U.S.A.) from the 16th to 19th October, 1961. On this occasion, will also be held the Statutory General Assembly of the IOVST as well as an international exhibition of vacuum equipment.

From now on it can be foreseen that both the Congress and the Exhibition will meet very great success.

Our Secretariat has sent to the members of IOVST outside the U.S.A., various documents relative to the Congress (registration form, advance programme, list of hotels, hotel reservation card). These documents have been sent to the members of the U.S.A. by the American Vacuum Society.

Those of our members who wish to take part in the Congress are kindly requested to register without delay, if this has not already been done.

The Transactions of the Congress will be published by Pergamon Press in two volumes containing a total of well over 1000 pages ; Transactions *ordered at the meeting* are $35.00.

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Wie erinnern daran, dass dieser Kongress, der von der American Vacuum Society (AVS) organisiert und unter der Schirmherrschaft der IOVPT abgehalten wird, vom 16. bis 19. Oktober 1961 im Sheraton-Park Hotel in Washington, D.C. (U.S.A.) stattfindet. Bei dieser Gelegenheit wird die Generalversammlung der IOVPT und eine internationale Vakuumausstellung abgehalten.

Man kann schon mit Bestimmtheir sagen, dass der Kongress und die Ausstellung einen grossen Erfolg haben werden.

Durch unser Sekretariat sind den Mitgliedern der IOVPT, die nicht in den Vereinigten Staaten wohnen, verschiedene Dokumente bezüglich des Kongresses (Mitgliedskarte, Vorprogramm, Hotelliste, Karte für Hotelreservierung) zugegangen. Diese Unterlagen sind unseren Mitglieder in den Vereinigten Staaten von der AVS zugeschickt worden.

Mitglieder, die an diesem Kongress teilnehmen möchten, werden gebeten, sich ohne Verzug anzumelden, sofern sie es nicht schon vorgenommen haben.

Berichte des Kongresses werden durch Pergamon Press in zwei Bänden mit insgesamt über 1000 Seiten veröffentlicht und kosten $35.00, wenn sie anlässlich des Kongresses bestellt werden.

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2. Annuaire de l'OISTV
Directory of the IOVST
Jahres-Handbuch der IOVPT

L'Annuaire de l'OISTV paraîtra dans le courant de l'automne 1961.

Envoyé gratuitement aux membres en règle de cotisation, il comprendra :

(a) les renseignements (nom, adresse, activités) concernant les membres collectifs ainsi que les membres individuels,

(b) les informations relatives à l'activité de l'Organisation.

Le Secrétariat a demandé aux membres de lui faire connaître les modifications à apporter éventuellement aux renseignements fournis lors de l'inscription. Nous prions nos membres qui n'auraient pas encore répondu à cet appel, de vouloir bien le faire de toute urgence.

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The Directory of the IOVST will be published in the course of Autumn 1961.

It will be sent free of charge to the members who have paid their dues and will include :

(a) information (name, address, activities) concerning the associate and the individual members ;

(b) information on the activity of the Organization.

The Secretariat has requested the members to inform it of any modification which should be brought to the information they gave when they applied for membership. The members who have not yet answered this request are kindly reminded to do it urgently.

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Das Jahres-Handbuch der IOVPT erscheint im Laufe des Herbstes 1961.

Es wird unentgeldlich den Mitgliedern zugeschickt, deren Beitrag bei uns eingegangen ist und enthält :

(a) Auskünfte (Name, Adresse, Tätigkeit) sowohl über Gruppen- wie auch über Einzelmitglieder ;

(b) Informationen über die Tätigkeit der Organisation.

Das Sekretariat hat unsere Mitglieder gebeten, eventuelle Änderungen, die seit ihrer Einschreibung vorgekommen sind, mitzuteilen. Wir ersuchen die Mitglieder, die dahingehend noch nicht geantwortet haben, es so schnell wie möglich nachholen zu wollen.

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3. Publications de l'UNESCO
UNESCO publications
Publikationen der UNESCO

Nous référant à l'information parue dans notre Bulletin No. 5 (page 12), nous avons le plaisir de reproduire ci-après une note de l'Unesco relative à la publication d'une très importante étude préparée sous la direction du Professeur Pierre AUGER.

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With reference to the information published in our Bulletin No. 5 (page 12), we have pleasure in reproducing below a note from Unesco concerning the publication of a very important study prepared under the direction of Professor Pierre AUGER.

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Wir verweisen auf die Bekanntmachung in unserem Informationsblatt Nr. 5 (S.12) und zitieren nachstehend einen Hinweis der Unesco über die Publikation einer sehr wichtigen Studie, die unter Leitung von Professor Pierre AUGER abgefasst wurde.

Tendances Actuelles de la Recherche Scientifique

par le Professeur PIERRE AUGER

En 1960 l'Assemblée générale des Nations Unies décida qu'une étude devait être faite sur les tendances actuelles de la recherche scientifique, sur la diffusion des connaissances scientifiques et leur application à des fins pacifiques. Le professeur Pierre Auger, éminent physicien et ancien directeur du Département des Sciences exactes et naturelles de l'Unesco, fut chargé par le Secrétaire général des Nations Unies et le Directeur général de l'Unesco de réunir les informations et de rédiger le rapport. 29 organisations intergouvernementales, 66 organisations internationales non-gouvernementales et les organisations nationales de recherche de 42 pays ont été consultées. De plus, les experts scientifiques de tous les pays ont été consultés à titre individuel.

Le professeur Auger se heurtait d'emblée à de nombreuses difficultés, d'abord celles qui résultaient du caractère essentiellement transitoire des renseignements à donner. Si le contenu de la science change assez vite, le type de recherches en cours risque de changer encore plus vite, celles-ci étant soumises à toutes sortes d'influences, matérielles ou intellectuelles, expérimentales ou théoriques. Ensuite, il est plus difficile de se procurer ce type de renseignements, qui ne sont pas en général rendus publics par les chercheurs et les laboratoires, ceux-ci préférant ne publier que les résultats achevés. Il était tout aussi indispensable d'analyser les facteurs sous l'influence desquels se sont produits récemment

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et une multiplication des disciplines particulières et un effort de synthèse inter-disciplinaire ; on ne pouvait oublier d'autre part que toute description de la recherche scientifique qui séparerait d'une façon absolue la science pure de la science appliquée fausserait le jeu naturel entre la connaissance et l'action. Enfin, le plan même adopté dans le corps du rapport, s'inspirant en gros de la classification d'Auguste Comte, n'en rassemble pas moins des sujets pris en divers points de cette classification, si par exemple ce groupement correspond à une grande préoccupation de l'humanité.

Les recommandations formulées en conclusion de cet ouvrage portent aussi bien sur la politique scientifique des Etats, que sur les champs d'activité à élargir. Pour reprendre une expression du professeur Auger, " quand un navire donne sa position, il indique sa latitude et sa longitude, puis il ajoute : faisant route au nord, vitesse 12 noeuds ".

Le plan général de l'enquête est basé sur une division fonctionnelle de la recherche scientifique, plutôt que sur une classification des sciences de caractère académique. Une telle classification, établie par le Comité consultatif spécial, suit les besoins de l'homme et correspond par le fait même aux structures institutionnelles de la recherche scientifique les plus fréquemment adoptées au niveau national et international. Elle offre donc l'avantage d'une répartition aisée des matières traitées entre les diverses institutions de recherche orientée, dans lesquelles l'applicabilité des résultats de la recherche conditionne pour une large part les efforts consentis. Tel est le cas par exemple de la recherche médicale, de la recherche agronomique, de la recherche sur l'énergie nucléaire.

Le rapport se divise en trois parties : La première : Les tendances principales de la recherche scientifique, a six chapitres principaux : I—Les sciences fondamentales ; II—Sciences de la terre et des espaces extra-terrestres ; III—Sciences médicales ; IV—Sciences de l'alimentation et de l'agriculture ; V—Combustibles et énergie ; VI—Recherche industrielle. La deuxième partie traite des tendances générales dans l'organisation de la recherche scientifique et la diffusion des résultats, et la troisième des recommandations générales et spéciales concernant la recherche scientifique, la diffusion des connaissances scientifiques et leur mise en application à des fins pacifiques. Les trois parties sont précédées d'une longue introduction du professeur Auger.

Le livre n'est pas seulement le premier en son genre, il sera probablement aussi un des ouvrages scientifiques de base les plus importants des dix années à venir. Cet ouvrage est d'un intérêt exceptionnel pour les institutions de recherche scientifique, pour les universités, les fonctionnaires chargés de questions scientifiques, les professeurs et pour l'industrie, ainsi que pour tous ceux qui s'intéressent à l'histoire et au développement des sciences.

17,50 NF
Paraîtra en juillet 1961

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Current Trends in Scientific Research

by Professor PIERRE AUGER

IN 1960, the General Assembly of the United Nations decided that a survey should be made on current trends of enquiry in the fields of the natural sciences and the dissemination and application for peaceful ends of such scientific knowledge. The Secretary-General of the United Nations and the Director-General of Unesco jointly appointed Professor Pierre Auger, a leading physicist, formerly head of the Unesco Natural Sciences Department, to collect data and draft the report. Twenty-nine intergovernmental organisations, sixty-six international non-governmental organisations and scientific unions, and the national research organisations of forty-two countries were consulted. The list of experts consulted in their individual capacity contains the names of leading scientists in all countries of the world.

Professor Auger faced a number of difficulties. These in the first place resulted from the essentially transitory nature of the required information. If the content of scientific knowledge is undergoing fairly rapid changes, the types of current enquiry are likely to change even more swiftly, since they are subject to influences of all kinds, whether material or intellectual, empirical or theoretical. Furthermore, it is difficult to gain access to this type of information, which as a general rule is not made known by scientists and laboratories, who prefer to publish only the results obtained. Then the problem arose of the method to be adopted. It was deemed wise to consider not only the factors responsible for the multiplication of specialized disciplines but also the opposite movement towards synthesis. Nor could one forget that any description of scientific research which drew a hard and fast line between pure and applied science would distort the natural interplay between knowledge and action. Eventually, the actual plan adopted in the body of the report broadly follows the classification of Auguste Comte, but groups together subjects from various parts of this classification where such a grouping, for instance, corresponds to a major concern of mankind.

The proposed measures with which the report concludes relate as much to the scientific policy of governments as to the fields which deserve broader action or better coordination. To quote from Professor Auger : " When a ship reports its position, it gives first its latitude and longitude, and then adds : steaming north at 12 knots ".

The general outline of the survey is based on a functional division of scientific research rather than on a purely academic classification of sciences. A classification of this type, as prepared by the Special Advisory Committee, reflects man's needs and accordingly corresponds to the institutional structures usually adopted for scientific research at the national and international level. The topics covered can thus easily be divided among the different institutions engaged in applied research, whose work depends to a great extent on the use to be made of the research results. This applies, for example, to medical and agricultural research, research on nuclear energy, etc.

The book is divided into three parts : Part One, " Trends of scientific research ", has six main chapters : I—Fundamental sciences ; II—The earth and space sciences ; III—Medical sciences ; IV—Food and agricultural sciences ; V—Fuel and power research ; VI—Industrial research.

Part Two deals with the main trends affecting the organisation of scientific research and the dissemination of results, and Part Three, general and special recommendations concerning scientific research, the dissemination of scientific knowledge and the application of such knowledge to physical needs. These three parts are preceded by a long introduction by Professor Auger.

This book is not only the first of its kind, but is also likely to be one of the most important basic scientific works of the coming decade. It will be of exceptional interest to science research institutions, universities, government science officers, science teachers, and also to state- and privately-owned industry and to all who are interested in the history and development of science.

33s. $6.75.
Ready 15 July 1961.

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Gegenwärtige Tendenzen der wissenschaftlichen Forschung

von Professor PIERRE AUGER

Die Generalversammlung der Vereinten Nationen beschloss 1960 die Anfertigung eines Berichtes über die gegenwärtigen Tendenzen der wissenschaftlichen Forschung, die Verbreitung wissenschaftlicher Erkenntnisse und ihre Anwendung zu friedlichen Zwecken. Professor Pierre Auger, ein bedeutender Physiker und ehemaliger Direktor des " Département des Sciences exactes et naturelles " der Unesco, wurde von dem Generalsekretariat der Vereinten Nationen und dem Generaldirektor der Unesco beauftragt, die notwendigen Informationen zusammenzutragen und den Bericht zu verfassen. 29 zwischenstaatliche Organisationen, 66 internationale, nicht staatliche Organisationen sowie die nationalen Forschungsinstitute von 42 Ländern wurden befragt. Darüber hinaus wurden die Wissenschaftler der Länder persönlich befragt.

Professor Auger stieff zunächst auf eine Vielzahl von Schwierigkeiten und vornehmlich auf jene, die auf dem vorläufigen Charakter der Informationen beruhten. Wenn der Gegenstand der Wissenschaft sich schnell ändert, ändert sich die Art der laufenden Untersuchungen womöglich noch schneller, da sie, sei es materiellen, konzeptionellen, experimentellen oder theoretischen Einflüssen unterworfen sind. Ausserdem ist est äusserst schwierig, sich derartige Auskünfte zu verschaffen, da sie im allgemeinen nicht von Forschern oder Laboratorien, die lieber abgeschlossene Ergebnisse veröffentlichen, bekanntgegeben werden. Es ist weiterhin unumgänglich, die Determinanten zu untersuchen, die sich seit kurzem auswirken und einerseits eine Aufspaltung der einzelnen Forschungsrichtungen und andererseits die Notwendigleit der Zusammenfassung verschiedener Disziplinen zu analysieren. Darüber hinaus darf man nicht vergessen, dass jede Darstellung der wissenschaftlichen Forschung, die streng die reine Theorie von der angewandten Wissenschaft trennt, die natürliche Beziehung zwischen Theorie und Praxis verfälscht. Obgleich sich die Gliederung, die dem Bericht zugrunde gelegt wurde, im allgemeinen stark an diejenige von Auguste Comte anlehnt, sind doch solche Themen, die an verschiedenen Stellen dieser Einteilung enthalten sind, zusammengefasst, wenn sie von grossem allgemeinen Interesse für die Menschheit sind.

Die Empfehlungen, die am Ende der Untersuchung gegeben werden, erstrecken sich sowohl auf die Forschungspolitik des Staates wie auf die auszudehnenden Untersuchungen. Um Professor Auger zu zitieren : " Wenn ein Schiff seine Position meldet, gibt es seine geographische Höhe und Breite an und fügt hinzu : fahre Richtung Norden, Geschwindigkeit 12 Knoten ".

Der allgemeine Gang der Untersuchung beruht eher auf einer funktionellen Einteilung der wissenschaftlichen Forschung als auf einer akademischen Klassifikation der Wissenschaften. Diese von dem Komitee der Sonderberater erstellte Einteilung entspricht den menschlichen Bedürfnissen und der von nationalen und internationalen Organisationen am häufigsten angewandten institutionellen Organisation der wissenschaftlichen Forschung. Dies hat den Vorteil einer einfachen Verteilung der behandelten Gebiete auf die verschiedenen Forschungsanstalten. Hierbei bestimmte die Anwendbarkeit der Ergebnisse weitgehend das Ausmass der Ausführlichkeit. Dies trifft z.B. für die Gebiete der Medizin, der Landwirtschaft und der Kernenergie zu.

Der Bericht besteht aus drei Teilen. Der erste Teil, der sich mit den Haupttendenzen der wissenschaftlichen Forschung beschäftigt, enthält die folgenden sechs Kapitel :

I. Hauptwissenschaften

II. Wissenschaften der Erde und des Weltraumes

III. Medizin

IV. Ernährungswissenschaft und Landwirtschaft

V. Brennstoffe und Energie

VI. Industrielle Forschung

Der zweite Teil schildert die allgemeinen Tendenzen bei der Organisation der wissenschaftlichen Forschung und der Verbreitung der Ergebnisse, während der dritte Teil die allgemeinen und speziellen Empfehlung hinsichtlich der wissenschaftlichen Forschung, der Verbreitung der wissenschaftlichen Erkenntnisse und ihre Anwendung für friedliche Zwecke enthält. Diese drei Teile werden durch ein langes Vorwort von Professor Auger eingeleitet.

Dieses Buch ist nicht nur das erste in seiner Art, sondern wird wahrscheinlich auch in den nächsten zehn Jahren eines der bedeutendsten wissenschaftlichen Standardwerke bleiben. Dieses Werk ist für wissenschaftliche Forschungsinstitute, Universitäten, Leute, die mit wissenschaftlichen Fragen zu tun haben, Lehrer und die Industrie sowie für alle, die sich für die Geschichte und Entwicklung der Wissenschaften interessieren, von ausserordentlicher Bedeutung.

Preis : 17,50 NF.
Erscheint ab Juli 1961.

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4. Groupes nationaux du vide
National vacuum groups
Nationale Vakuum-Gruppen

A. Deutscher Arbeitskreis Vakuum (DAV)

Am 20.IV.1961 fand in Bad Nauheim eine Vortragsveranstaltung für Vakuum-Interessenten statt, bei der die folgenden Themen behandelt wurden :

Le 20 avril 1961 a eu lieu à Bad Nauheim un symposium consacré aux sciences et techniques du vide et au cours duquel les sujets suivants ont été traités :

A symposium on vacuum sciences and techniques has been held in Bad Nauheim on the 20 April 1961. The following topics have been discussed :

(1) Degras und A. Schram, Centre d'Etudes Nucléaires de Saclay, France :
" Anomalies observées sur certains modes de pompage et de mesure de basses pressions en milieu hydrogéné "
(vorgetragen von A. Schram)

(2) Dr. Nöller, E. Leybold's Nachfolger, Köln :
" Probleme bei der Messung sehr niedriger Drucke "

(3) Dr. Reich, E. Leybold's Nachfolger, Köln :
" Die Messung sehr niedriger Drucke mittels der Desorptions-methode "

(4) R. A. Haefer und J. Hengevoss, Balzers AG, Balzers (Liechtenstein) :
" Zur Frage der Molekularströmung von Öldämpfen durch Rohrleitungen "
(vorgetragen von J. Hengevoss)

(5) Dr. Kienel, W. C. Heraeus GmbH, Hanau (Main) :
" Erfahrungen beim Bau von Ultrahoch-Vakuumanlagen "

(6) Dr. S. Garbe, Philips Zentrallaboratorium, Aachen :
" Gasabgabe von Gläsern "

(7) G. Rauscher und G. Staudt, Physikalisches Institut der Universität Tübingen, Tübingen :
" Die Wasserstoffabsorption von Bariumgettern im Druckbereich von 10^{-4} bis 10^{-3} Torr "
(vorgetragen von G. Rauscher)

(8) Dr. N. Hansen, Philips Zentrallaboratorium Aachen :
" Adsorption von Gasen an Zirkonium bei tiefen Temperaturen "

(9) Dr. Hoch, E. Leybold's Nachfolger, Köln :
" Ausheizbare Verbindungen an Hochvakuum-Apparaturen "

(10) K. G. Müller, W. C. Heraeus GmbH, Hanau (Main) :
" Ein Verfahren zum Fernhalten korrosiver oder kondensierbarer Gase bzw. Dämpfe von Druckmeszeinrichtungen im Grobvakuum "

(11) Dr. K. G. Günther und Dr. W. Hänlein, Siemens-Schuckert-Werke AG, Laboratorium LS, Nürnberg :
" Das Vakuumthermoelement (thermionic converter) zur direkten Energie-Konversion "
(vorgetragen von Dr. K. G. Günther)

Im Anschluss an diese Vorträge wurde eine Sitzung abgehalten, auf der bekanntgegeben wurde, dass die drei Verbände,

DECHEMA, Deutsche Gesellschaft für Chemisches Apparatewesen e.V.
Verband Deutscher Physikalischer Gesellschaften (VDPG)
Verfahrenstechnische Gesellschaft (VTG) im Verein Deutscher Ingenieure

sich erboten haben, Träger und Gründer des

" Deutscher Arbeitskreis Vakuum (DAV) "

zu werden, wobei sie damit rechnen, dass noch weitere wissenschaftliche Verbände ebenfalls die Trägerschaft des DAV anzunehmen bereit sind.

Nachdem schon vorher die schriftliche Zustimmung von rund 300 natürlichen und juristischen Personen zu dieser Neugründung eingeholt war, wurde seitens der Versammlung der Gründungsbeschluss mit Beifall begrüsst.

Der Beirat des DAV setzt sich wie folgt zusammen :

Dr. D. Behrens, Frankfurt (Main)
Dr. H. Bretschneider, Frankfurt (Main)
Professor Dr. K. Diels, Köln
Professor Dr. H. Ebert, Braunschweig
Direktor Dipl.-Phys. H. Gruber, Hanau
Dr. sc. nat. W. Hänlein, Nürnberg
Dr.-Ing. G. Hermann, Ulm
Professor Dr. R. Jaeckel, Bonn
Dr. A. Klopfer, Aachen
Dr.-Ing. H. Mieszner, Leverkusen
Dr. rer. nat. G. W. Oetjen, Köln
Dr.-Ing. habil. W. Pupp, Wetzlar
Dr.-Ing. W. Scheibe, Wolfgang bei Hanau
Dr. K. Steimel, Frankfurt (Main)

Die anschliessende Vorstandswahl hatte das folgende Ergebnis :

Prof. Dr. H. Ebert—Braunschweig, Vorsitzender
Prof. Dr. K. Diels—Köln, stellvertretender Vorsitzender
Direktor Dipl.-Phys. J. Gruber—Hanau, stellvertretender Vorsitzender
Dr. sc. nat. W. Hänlein—Nürnberg, Vorstandsmitglied
Dr.-Ing. habil. W. Pupp, Vorstandsmitglied.

Weitere Unterrichtung erteilt sowie Anmeldungen nimmt entgegen :

Deutscher Arbeitskreis Vakuum (DAV)
Die Geschäftsstelle
Frankfurt (Main)—7
Rheingau-Allee 25

Au cours de l'assemblée qui a suivi ces conférences, il a été annoncé que les trois associations :

DECHEMA, Deutsche Gesellschaft für Chemisches Apparatewesen e.V.
Verband Deutscher Physikalischer Gesellschaften (VDPG)
Verfahrenstechnische Gesellschaft (VTG) im Verein Deutscher Ingenieure

s'étaient offertes à soutenir et à fonder le

" Deutscher Arbeitskreis Vakuum (DAV) ",
en espérant que d'autres organisations scientifiques étaient prêtes à soutenir également le DAV.

Au préalable, l'acquiescement écrit d'environ 300 personnes physiques et morales avait été recueilli. L'assemblée salua avec enthousiasme la constitution de la nouvelle association.

Le Conseil du DAV se compose comme suit :

Dr. D. Behrens, Frankfurt (Main)
Dr. H. Bretschneider, Frankfurt (Main)
Professor Dr. K. Diels, Köln
Professor Dr. H. Ebert, Braunschweig
Direktor Dipl.-Phys. H. Gruber, Hanau
Dr. sc. nat. W. Hänlein, Nürnberg
Dr.-Ing. G. Hermann, Ulm
Professor Dr. R. Jaeckel, Bonn
Dr. A. Klopfer, Aachen
Dr.-Ing. H. Mieszner, Leverkusen
Dr. rer. nat. G. W. Oetjen, Köln
Dr.-Ing. habil. W. Pupp, Wetzlar
Dr.-Ing. W. Scheibe, Wolfgang bei Hanau
Dr. K. Steimel, Frankfurt (Main).

Les élections du bureau ont donné les résultats suivants :

Professor Dr. H. Ebert—Braunschweig, Président
Professor Dr. K. Diels—Köln, Vice-Président
Direktor Dipl.-Phys. H. Gruber—Hanau, Vice-Président
Dr. sc. nat. W. Hänlein—Nürnberg, Membre
Dr.-Ing. habil. W. Pupp, Membre.

Des renseignements complémentaires seront fournis par le
Deutscher Arbeitskreis Vakuum (DAV)
Die Geschäftsstelle
Frankfurt (Main)—7
Rheingau-Allee 25
qui recevra également les adhésions.

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It was announced at the meeting which followed this symposium that the three associations :

DECHEMA, Deutsche Gesellschaft für Chemisches Apparatewesen e.V.
Verband Deutscher Physikalischer Gesellschaften (VDPG)
Verfahrenstechnische Gesellschaft (VTG) im Verein Deutscher Ingenieure

had offered to support and constitute the
" Deutscher Arbeitskreis Vakuum (DAV) ",
with the hope that other scientific organizations were equally ready to support the DAV.

Previously, the written consent of approximately 300 persons and corporate bodies had been collected. The meeting greeted enthusiastically the constitution of the new association.

The Committee of the DAV is composed as follows :

Dr. D. Behrens, Frankfurt (Main)
Dr. H. Bretschneider, Frankfurt (Main)
Professor Dr. K. Diels, Köln
Professor Dr. H. Ebert, Braunschweig
Direktor Dipl.-Phys. H. Gruber, Hanau
Dr. sc. nat. W. Hänlein, Nürnberg
Dr.-Ing. G. Hermann, Ulm
Professor Dr. R. Jaeckel, Bonn
Dr. A. Klopfer, Aachen
Dr.-Ing. H. Mieszner, Leverkusen
Dr. rer. nat. G. W. Oetjen, Köln
Dr.-Ing. habil. W. Pupp, Wetzlar
Dr.-Ing. W. Scheibe, Wolfgang bei Hanau
Dr. K. Steimel, Frankfurt (Main).

The following results were recorded at the elections of the Board :

Professor Dr. H. Ebert—Braunschweig, President
Professor Dr. K. Diels—Köln, Vice-President
Direktor Dipl.-Phys. H. Gruber—Hanau, Vice-President
Dr. sc. nat. W. Hänlein—Nürnberg, Member
Dr.-Ing. habil. W. Pupp, Member.

Complementary information will be supplied by the
Deutscher Arbeitskreis Vakuum (DAV)
Die Geschäftsstelle
Frankfurt (Main)—7
Rheingau-Allee 25
which will also receive the applications for membership.

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B. Asociacion Argentina Para la Cienca Y Técnica del Vacio (ACITEV)

Le 4 novembre 1960 a été fondée l'Asociacion Argentina Para la Cienca Y Técnica del Vacio (ACITEV). Le siège social est :

Instituto de Física de la Universidad Nacional de La Plata, Calle 1, esquina 47, La Plata, Prov. de Buenos Aires, Argentina.

The Asociacion Argentina Para la Cienca Y Técnica del Vacio (ACITEV) was established on the 4th November, 1960. Its Registered Office is :

Instituto de Física de la Universidad Nacional de La Plata, Calle 1, esquina 47, La Plata, Prov. de Buenos Aires, Argentina.

Am 4. November 1960 wurde die Asociacion Argentina Para la Cienca Y Técnica del Vacio (ACITEV) gegründet. Sie hat ihren Sitz in :

Instituto de Física de la Universidad Nacional de La Plata, Calle 1, esquina 47, La Plata, Prov. de Buenos Aires, Argentina.

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5. Liste des nouveaux membres fondateurs de l'OISTV allant du 26 septembre 1960 au 30 juin 1961

List of the new founder members of the IOVST, as from September 26, 1960 to June 30, 1961

Liste der neuen Gründer-Mitglieder der IOVPT vom 26. September 1960 bis 30. Juni 1961

La liste suivante comprend les noms des nouveaux membres fondateurs classés selon le pays où ils résident :

The following list contains the names of the new founder members who are classified according to their present residing State :

Die nachfolgende Liste umfasst die Namen der neuen Gründer-Mitglieder, eingeteilt nach dem Lande ihres gegenwärtigen Wohnsitzes :

MEMBRES FONDATEURS COLLECTIFS
ASSOCIATE FOUNDER MEMBERS
KOLLEKTIVE GRÜNDER-MITGLIEDER

Etats-Unis—U.S.A.—V.S. von Nordamerika

Vactronic Lab. Equipment, Inc., East Northport, N.Y.
(Delegate : Mr. ROBERT A. MORRIS, Sales Manager)
Vacuum Engineering Company, North Billerica, Massachusetts
(Delegate : Mr. PETER ZERIGIAN, President)

MEMBRES FONDATEURS INDIVIDUELS
INDIVIDUAL FOUNDER MEMBERS
INDIVIDUELLE GRÜNDER-MITGLIEDER

Allemagne (Rép. Féd.)—Germany (Fed. Rep.)—Deutschland (Bundesrepublik)

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FLECKEN, Dr., Köln-Bayental.

Belgique—Belguim—Belgien

J. Z. J. CLAESEN, Chef de Service, Bruxelles.
Florent PEETERS, Administrateur-Gérant, Bruxelles 4.
A. PROCUREUR, Chef de Service, Watermael-Bruxelles.
Robert RUIDANT, Technicien, Salzinnes.
André VAN BOKESTAL, Ing. Techn. Chimiste, Bruxelles 7.

Etats-Unis—U.S.A.—V.S. von Nordamerika

Carl ALTMAN, Dr., Princeton, N.J.
B. R. BEARD, Exec. Vice-President, Hayward, California.
Jack H. BURTHE, Engineer, Baltimore, Maryland.
James M. CAMERON, Mech. Engineer, Utica, N.Y.
Paul Euclide DALBEC, M. of S., Woonsocket, Rhode Island.
Eubert J. DANIEL, Dr., Boston, Massachusetts.
Richard A. DENTON, Vice-President, Haddonfield, N.J.
Humbert A. D'ORAZIO, Technician, Philadelphia 4, Pennsylvania.
James H. EDDLESTON, Senior Proj. Eng., Richardson, Texas.
Harold ESTEN, Mech. Eng., West Chester, Pennsylvania.
Ivory P. S. FISH, Section Head, Burlington, Massachusetts.
Bob FRAZER, Scientist, La Canada, California.
Henry E. GARBUTT, Processes Eng., Baltimore, Maryland.
William D. HARMAN, Department Head, Oak Ridge, Tennessee.
Dan M. IHLE, Design Engineer, Lynn.
Charles E. JEANNE, Proj. Eng., Utica, N.Y.
Donald B. LEE, Sales Executive, Cleveland 12, Ohio.
Richard G. MAGUIRE, Assoc. Chemist, Chicago 20, Illinois.
John T. MARK, Chief Engineer, Lancaster, Pennsylvania.
George L. MCGINNESS, Jr., West Hartford 10.
Loren PATRICK, Mech. Engineer, Alhambra, California.
Lynn E. PAUL, Assoc. Res. Eng., Ann Arbor, Michigan.
S. H. PETRY, Chief Engineer, Chicago 10, Illinois.
Michael RIVERA, Manager, Palo Alto, California.
Thomas J. SCALA, President, Livingston, N.J.
D. R. SCHINDLER, Engineer, East Cleveland 12, Ohio.
Rudolph G. STEINER, Eng. Technician, Silver Spring, Maryland.
Richard R. STONE, Assoc. Chemist, Endicott, N.Y.
Jack TEALE, Techn. Specialist, Pleasant Valley, N.Y.
Robert WARNER, Elect. Engineer, Chicago, Illinois.
David B. WEBB, Manager, Berkeley 10, California.

Japon—Japan

Chikara HAYASHI, Dr., Yokohama.
Hideo SIBATA, Director, Yokohama.

Nouvelle Zélande—New Zealand—Neuseeland

John HAWTHORN, Director, Whangarei, Northland.

Royaume-Uni—United Kingdom—Grossbritannien

Tom E. LUCAS, Chief Engineer, Cambridge.

Suède—Sweden—Schweden

Mats RYDINGER, M. of S., Västerås.
Erik SJÖSTRAND, Bergsingenjör, Stockhom 70.
Pär G. STENBERG, Näsby-Park.
Herbert F. STEYSKAL, Dr. Ing., Stockhom 80.
Henry WALLMAN, Professor, Göteborg.

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H. ADAM, Köln-Bayenthal, Deutschland, Bundesrepublik.
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A. PIGUET, Pirbright, United Kingdom.
R. SAS, Halifax, Canada.
Mme N. VANDER LINDEN-BAUWENS, Alsemberg, Belgique.

Nous saurions gré aux membres changeant d'adresse ou de fonction de bien vouloir nous en aviser le plus rapidement possible. Ils faciliteront ainsi la tâche du Secrétariat.

We would be obliged if members changing their address or function would kindly advise us of same as quickly as possible. They will in this way facilitate the task of the Secretariat.

*
* *

Wir wären denjenigen Mitgliedern, welche ihre Adresse oder Funktion ändern verbunden, wenn sie uns hiervon so schnell wie möglich verständiden würden ; hierdurch wären die Arbeiten des Sekretariats wesentlich erleichtert.

TABLEAU RÉCAPITULATIF — GENERAL TABLE
ZUSAMMENFASSENDE TABELLE

Pays — Countries — Länder	Membres fondateurs collectifs Associate founder members Kollektive Gründer-Mitglieder	Membres fondateurs individuels Individual founder members Individuelle Gründer-Mitglieder
Org. europ.—Europ. Org.	1	2
Allemagne—Germany—Deutschland :		
Rép. Dém.—Dem. Rep.	1	3
Rép. Féd.—Fed. Rep.—Bundesrep.	6	36
Argentine—Argentinien		2
Australie—Australia—Australien		9
Autriche—Austria—Österreich		1
Belgique—Belgium—Belgien	14	57
Brésil—Brazil—Brasilien		2
Canada		9
Danemark—Denmark—Dänemark		1
Espagne—Spain—Spanien	1	5
Etats-Unis—U.S.A.—V.S. von Amerika	15	321
France—Frankreich	1	12
Hongrie—Hungary—Ungarn		4
Inde—India—Indien		1
Israël		2
Italie—Italy—Italien	2	5
Japon—Japan	3	7
Liechtenstein	1	4
Norvège—Norway—Norwegen		2
Nouvelle Zélande—New Zealand—Neuseeland		1
Pays-Bas—Netherlands—Niederlande	1	7
Philippines—Philippinen		1
Pologne—Poland—Polen		1
Royaume-Uni—U.K.—Grossbritannien	4	29
Suède—Sweden—Schweden		7
Suisse—Switzerland—Schweiz		11
Tchécoslovaquie—Czecho-Slovakia—Tschechoslowakei		2
Yougoslavie—Yugoslavia—Yugoslavien		3
	50	548

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6. Lettres à l'éditeur
Letters to the editor
Briefen an den Herausgeber

Souffleries Roots—Pompes Roots

L'EMPLOI des pompes à vide Roots, ainsi appelées parce qu'elles fonctionnent suivant le principe des souffleries Roots, n'a cessé de se développer au cours de ces dernières années.

Toutefois, comme l'origine de ces souffleries est généralement ignorée de ceux qui s'intéressent aux sciences et techniques du vide, elle mérite d'être retracée en quelques mots.

Une brochure publiée en 1954 par la Société Roots-Connersville Blower—A Division of Dresser Industries Inc., Connersville, Indiana (E.-U. d'Amérique) nous apprend que, cent ans plus tôt, les frères Philander H. et Francis M. ROOTS découvrirent d'une manière toute fortuite le principe qui porte leur nom.

A cette époque, ils possédaient à Connersville une filature de laine dont la force motrice était fournie par le Whitewater Canal. Dans l'espoir d'augmenter le rendement de leur filature, ils substituèrent à la roue hydraulique une machine constituée par deux palettes tournant en sens inverse l'une de l'autre dans un carter. Ce fut un échec mais ils remarquèrent que tant que les palettes tournaient, de l'air s'échappait de l'orifice de refoulement.

Ils songèrent dès lors à employer leur machine comme soufflerie dans une fonderie. Cette fois, leur tentative réussit et les incita à entreprendre la construction de souffleries.

Pour terminer, disons que le nom des inventeurs n'est pas toujours écrit correctement ; on trouve en effet " ROOT " et même " ROOTES " dans des livres, des manuels, des dictionnaires techniques. La forme " ROOTES " est manifestement erronée.

L'origine de l'autre forme s'explique aisément, l's terminal du nom ROOTS ayant été considéré par certains comme la marque du génitif.

*
* *

Roots blowers. Roots pumps

THE use of Roots vacuum pumps, so called because they work according to the Roots blowers principle, has not ceased to extend during recent years.

However, since the origin of these blowers is generally unknown to those who are interested in vacuum sciences and techniques, it deserves to be related here in a few words.

A pamphlet published in 1954 by Roots-Connersville—A Division of Dresser Industries Inc., Connersville, Indiana (U.S.A.) tells us that a hundred years ago, the Philander H. and Francis M. ROOTS brothers unexpectedly discovered the principle which bears their name.

In those days they had in Connersville a woollen mill for which power was derived from the Whitewater Canal. Hoping to increase the efficiency of their mill, they substituted for the water wheel a machine composed of two paddles, both revolving in a casing in opposite directions. It was a failure, but they noticed that while the paddles were revolving a stream of air issued from the outlet.

They then thought to use their machine as a blower in a foundry. This time their attempt succeeded and instigated them to undertake the construction of blowers.

To conclude, let us say that the name of the inventors is not always correctly spelt ; we find " ROOT " and even " ROOTES " in books, handbooks and technical dictionaries. The spelling " ROOTES " is undoubtedly wrong. The origin of the first spelling can easily be explained, the last

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letter of ROOTS being sometimes considered as the " s " of the genitive case.

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* *

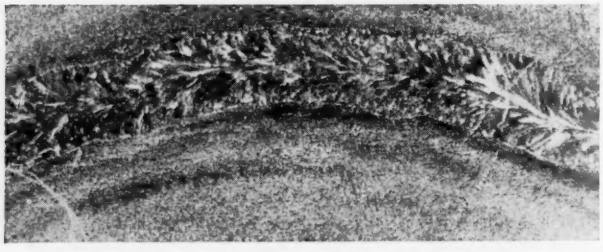
Un Traitement simple améliorant les Soudures à l'Arc sous Argon des Aciers inoxydables

LA RÉALISATION de pièces en acier inoxydable destinées à un groupe de pompage d'ultra-vide demande un soin tout particulier lors de l'exécution des soudures. Une série d'essais effectués dans l'atelier de notre laboratoire nous a permis de constater qu'un traitement très simple des pièces améliore sensiblement les conditions de soudage et les propriétés de la pièce terminée. Les soudures ont été exécutées à l'arc continu sous argon (électrode de tungstène) sur une variété d'acier austénitique (C : 0,06% max., Cr : 17%, Ni : 11,5% à 12,5%, Mo : 2,5% à 2,8%, $R_r = 60$ kgf/mm²).

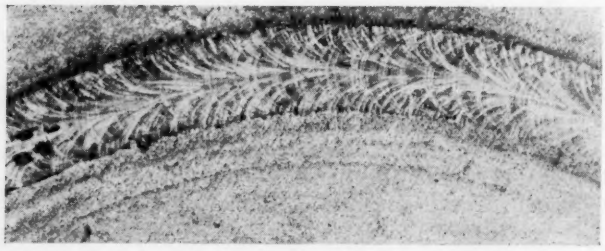
Le traitement consiste à préparer les pièces par :

(1) une mise sous vide (environ 50 mTorr, durée : 2 h) ;

(2) une mise sous argon (100 Torr, durée : 15 min) ;



(a) Echantillon de soudure sur pièce non traitée. Remarquer l'irrégularité des grains et des bords de la soudure.



(b) Echantillon de soudure sur pièce traitée. Le cordon est plus régulier en grains et en forme.

FIG. 1. Aspect du cordon de soudure.

(a) Pièce non traitée.

(b) Pièce traitée.

FIG. 2. Oxydation du côté opposé à la soudure. Le noircissement de la photo est une indication du degré d'oxydation du métal.

(3) une remise à l'air, suivie de soudage par la technique habituelle (les pièces d'essais sont placées sur un support rotatif entraîné à vitesse constante, l'électrode est fixe, l'amorçage se fait au cuivre) ;

(4) une remise sous vide aussi rapide que possible après soudage.

Les divers essais effectués, nous ont permis de constater que ce traitement conduisait aux améliorations suivantes :

(1) Les cratères d'amorce et de fin d'arc sont très réduits. L'intensité en fin de soudage peut être sensiblement diminuée sans rupture d'arc, ce qui permet une réduction progressive de la zone de chauffe.

(2) L'arc est très stable et suit avec une grande régularité la trajectoire imposée (Fig. 1), ce qui évite les fissures et

criques provoquées par les sauts de l'arc d'une lèvre à l'autre de la soudure, et améliore certainement l'étanchéité. Cette stabilité semble due au remplacement de l'oxygène adsorbé par de l'argon. La régularité du cordon pourrait être due à l'absence d'eau en surface de la pièce. D'autre part, la distance pièce-électrode est moins critique ; elle peut varier sans rupture ni épanouissement de l'arc.

(3) Pour des soudures de mêmes caractéristiques (largeur et profondeur), on peut diminuer l'intensité d'environ 10%, ce qui réduit fortement la zone d'oxydation de part et d'autre de la soudure.

(4) La mise sous vide après soudage évite la formation de l'oxyde très noir observé généralement au refroidissement. L'oxydation dans la zone bleue est réduite et disparaît par simple brossage, alors que normalement, il reste une trace foncée sur le métal. La pièce refroidit moins vite, ce qui diminue les déformations.

(5) L'argon adsorbé par la pièce semble aussi contribuer à la diminution de l'oxydation pendant le soudage, ainsi que le montrent les photos de la Fig. 2.

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* *

Réalisation simple d'un Séparateur pour Pompes à Lest d'Air

Lors de l'emploi prolongé d'une pompe à vide rotative (surtout en cas d'utilisation fréquente du lest d'air), il convient d'évacuer à l'extérieur du local les gaz et vapeurs pompés, ainsi que les vapeurs d'huile. Afin de protéger la pompe des condensations qui se produisent dans la ligne d'évacuation, il faut donc prévoir un séparateur sur le refoulement.

On trouvera à la Fig. 1 les vues en coupe de deux modèles de séparateur utilisés sur les groupes de pompage de notre laboratoire. Les pièces sont de construction très simple, la paroi transparente permet un contrôle permanent du fonctionnement. Les dimensions du séparateur dépendent évidemment de la quantité de vapeur évacuée et de la fréquence des vidanges. Les matériaux utilisés pour la construction de la pièce dépendent de la nature des gaz et vapeurs pompés.

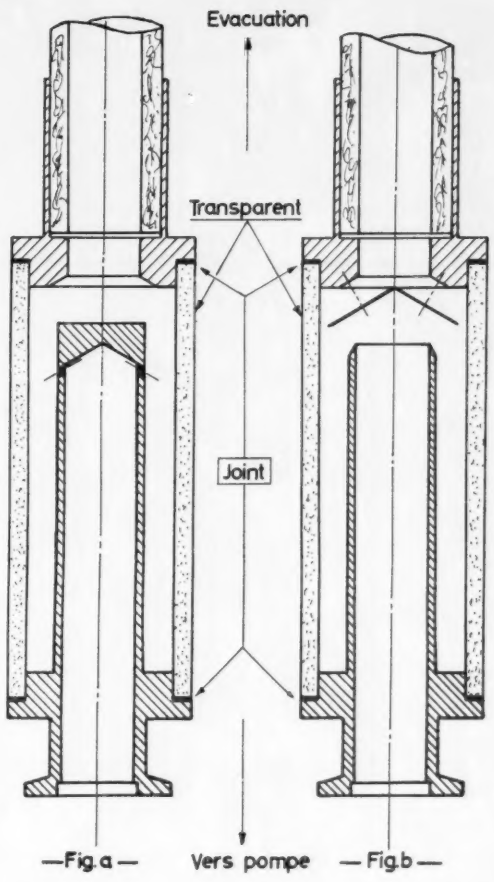

Fig. 1

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VACUUM

Papers to be published in future issues

J. H. Bloom, C. E. Ludington and R. L. Phipps. The Study of a Continuous Getter at High Ambient Temperatures with Carbon Dioxide.

W. Becker. Reibungsvakuummeter " REVA " ; " REVA " Friction Vacuum Gauge.

G. von Vick. Friction Effects in a Satellite Environment : The Present State of the Art.

VACUUM

The Study of a Continuous Getter at High Ambient Temperatures with Carbon Dioxide

J. H. BLOOM, CHARLOTTE E. LUDINGTON and R. L. PHIPPS
Air Force Cambridge Research Laboratories, ERD, L. G. Hanscom Field, Bedford, Mass, U.S.A.

An alloy of cerium–aluminum–thorium (CerAlloy 400) has been examined as a continuous getter in the temperature range from 400 to 1000°C to correlate and extend recent theoretical developments in the gettering field. The behavior of a continuous getter as a function of temperature and pressure is described. The experimental equipment and measurements reported here were specifically designed to permit the calculation of the diffusion constants, partition coefficients, and adsorption rates of continuous getters as a function of time, temperature and pressure. It has been concluded that the theory is of value in the interpretation of the behavior of high temperature continuous getters. A detailed examination of the data, however, reveals that some modifications must be made in the theory to account for the effects observed at very low pressures and very high temperatures.

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Introduction

The rapid advances recently made in electronic and engineering technologies have resulted in an increasing demand for electron tubes that are capable of reliable performance at high ambient temperatures. When conventional tubes are operated under these conditions, large quantities of sorbed gases are usually evolved resulting in cathode poisoning, changes in contact potential, and a consequent reduction in cathode emission. In addition, the high temperatures permit the migration of flash getter deposits which can contribute to interelectrode and heater cathode leakage. The combined effect is a sharp reduction in tube life with elevated temperatures. It has become increasingly apparent that new materials, techniques and configurations will be necessary to meet the demands of the new technologies.

It has been suggested that the problems associated with the evolution of gases trapped in tube components and the migration of flash getter deposits at elevated temperatures may be circumvented by using some form of a high temperature continuous getter, i.e. a getter that will adsorb gas rapidly and irreversibly throughout its life at high temperatures. An alloy of cerium–aluminum–thorium (CerAlloy 400)* has been suggested and successfully used for this application. This material, which is similar to the Ceto† getter, functions between 200 and 1000°C; it is reported to be most efficient in the 400–500°C range. Since the alloy is refractory in nature, there can be no metal migration at elevated temperatures which would result in electrical leakage. The capacities and adsorption rate of this material are such that it may even be used as an auxiliary pump to handle the large bursts of gas given off during cathode activation.

The principal purpose of the investigation reported herein was to correlate and extend the theory of Doucette[1, 2] under improved vacuum conditions.

Carbon dioxide was chosen as the test gas in these experiments because it is one of the residual gases most commonly found in large quantities in vacuum tubes.

Theoretical background

The action of high temperature getters is described as a diffusion limited process[3], characterized by the equation

$$\frac{P - P_f}{P_o - P_f} = \sum_{n=1}^{\infty} \frac{6S(1-S)}{9(1-S) - S^2 q_n^2} \exp[-q_n^2 Dt/r_o^2] \qquad (1)$$

where P_0 is the initial pressure of the system; P, the pressure at any time t; P_f is the final pressure in the system at infinite time; D, the diffusion constant; r_0 is the radius of the getter, and the q_n terms are solutions, positive and non-zero, of the equation[4]

$$\tan q_n = \frac{3q_n}{3 - Sq_n^2}. \qquad (2)$$

The effective volume ratio, S, is defined as

$$S = \frac{3V}{4\pi K r_o^2} \qquad (3)$$

where V is the volume of the system and K is the partition coefficient (sticking probability), describing the equilibrium conditions that must exist between the surface of the getter and the gas phase.

The theory also specifies that the final equilibrium pressure is determined by either the system leak rate (real or virtual), or a chemical compound dissociation pressure, and that the capacity of the getter is limited only by a nearly stoichiometric depletion of the gettering matter or alloy.

*Ronson Metals Corp., Newark, N.J. †Telefunken Laboratories, Germany.

Using equations (1), (2) and (3), one finds it possible to explain the behavior of continuous getters in the presence of various active gases when operated above 600°C. These gases include carbon monoxide, nitrogen, methane and hydrogen.

For the purposes of the investigation reported herein, Doucette was able to extend the theory further to include a definition of the gettering rate (Appendix). Using conventional units, one may define the rate of continuous getters :

$$S = \frac{DV \sum_{n=1}^{\infty} q_n^2 \exp[-q_n^2 Dt/r_0^2]}{r_0^2 \sum_{n=1}^{\infty} \exp[-q_n^2 Dt/r_0^2]}. \quad (4)$$

With use of equation (4) along with equations (1) through (3), an attempt will be made here to characterize the behavior of a continuous getter as a function of temperature and pressure. Particular attention will be given to some of the several assumptions, in order to illustrate their validity and the more subtle implications of the theory.

Experimental procedure

The experimental measurements reported here were specifically designed to permit the calculation of the diffusion constants, partition coefficients, and adsorption rates of continuous getter as a function of time and temperature. The changes in carbon dioxide pressure were continuously monitored with consistent and reproducible results in the isovolumetric system illustrated in Fig. 1.

Fig. 2 is a block diagram showing the functional relationship of the individual components of the system. Blocks 1, 2 and 3 represent the pumping mechanism that is capable of reducing the pressure to 3×10^{-9} Torr. Ultra-high vacuum bakeable metal valves were used so that the introduction of contaminants might be kept to a minimum. The valves were selected to provide a dead seal against gas flow when the pumps are operating at a pressure of 10^{-9} Torr and the system doped to a pressure in the order of 10^{-3} Torr. Valve 1 ($V1$) isolates the pumps from the remainder of the system.

The purpose of the ballast bulb (block 5) was to enlarge the volume of the system. Since the surface of a vacuum system may act as a weak getter or a virtual leak, a spherical

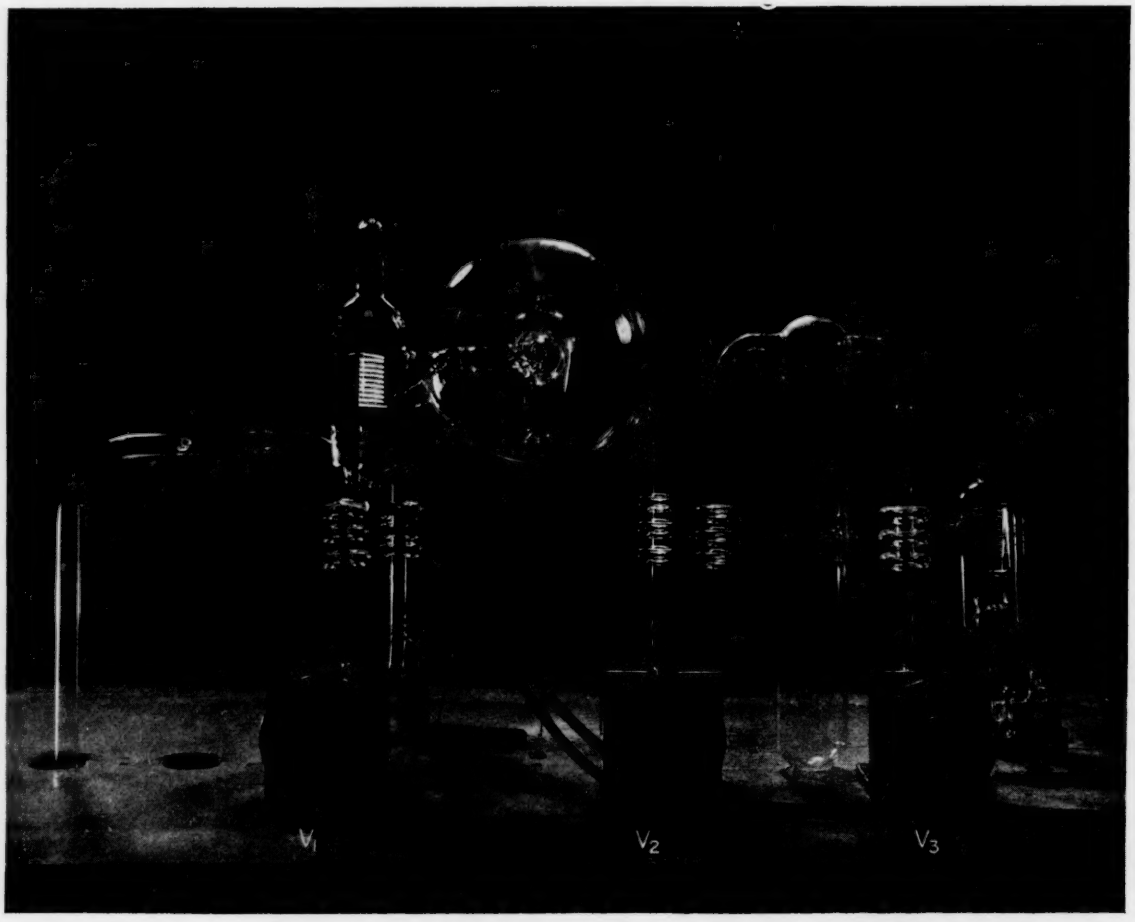

FIG. 1. Isovolumetric system.

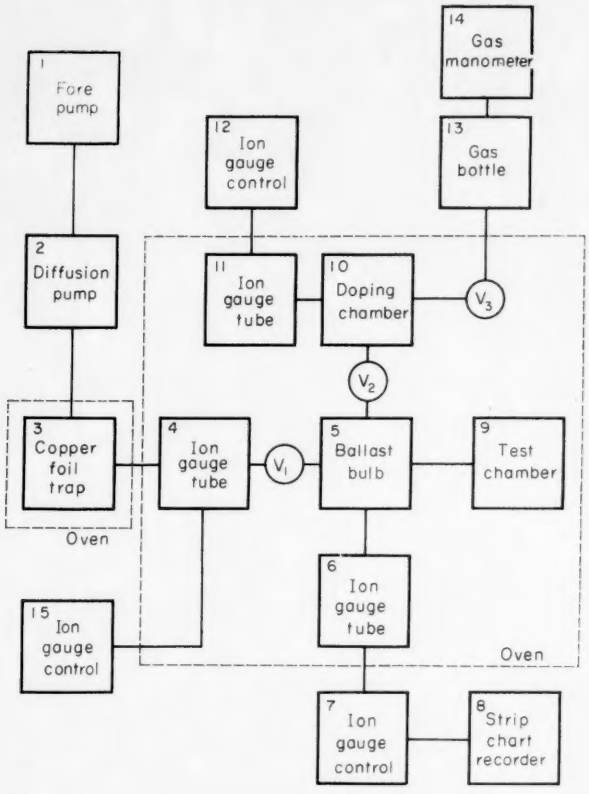

FIG. 2. A block diagram of the system.

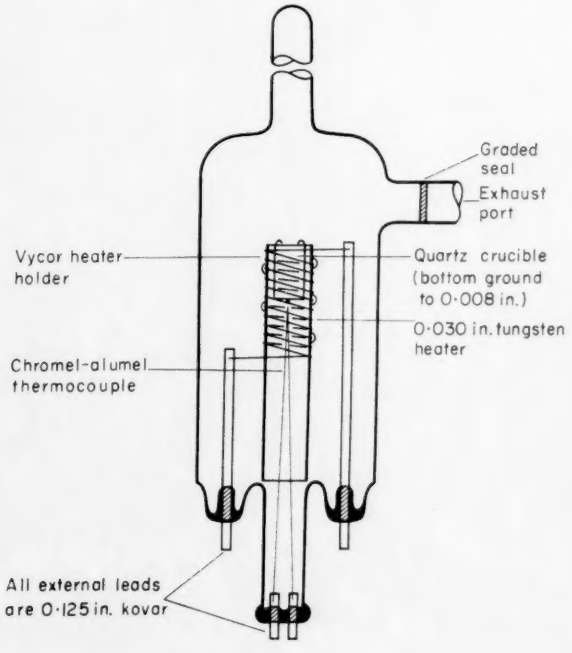

FIG. 3. Test chamber.

ballast bulb was chosen so that the smallest surface-to-volume ratio might be obtained.

Fig. 3 is a detail drawing of the test chamber and components (block 9). The getter sample was heated using a tungsten coil ; the temperature was measured with a chromel–alumel thermocouple, using a Leeds and Northrup potentiometer.

Veeco RG75 ionization gauges, which are essentially linear over the 10^{-3}–10^{-9} Torr range, were used to measure the pressure in the various parts of the system. Pressure data were constantly monitored on a strip chart recorder (block 8). The ion gauges were found to have a partial pumping action in spite of the attempt to saturate them with CO_2. Tests showed this effect to be secondary ; thus it was not computed in the data.

The doping chamber (block 10) provided a means of injecting a known quantity of gas into the system for the gettering tests. A 1 liter bottle of reagent grade CO_2 (block 13) supplied the gas for the tests. On termination of the gettering test, the gas manometer (block 14) measured the residual gas in the bottle.

One and a half grams of CerAlloy 400 powder, with a particle size of 15 μ, was pressed into a 0.625 cm diameter pellet at 1500 lb force, the pellet placed in the test chamber, and the entire system baked at 400°C for several hours. At this temperature, the best vacuum obtained before sintering the pellet was 2.2×10^{-4} Torr. (The temperature of the pellet measured about 300°C under these conditions). The sample was then slowly heated in 100° increments to the sintering temperature of 1000°C, and held there for $\frac{1}{2}$ hr.

With the sample at approximately 300°C and the vacuum system pumped to 3×10^{-9} Torr, the system was valved off. The pressure remained constant for 30 min before the experiment was started. This vacuum is an order of magnitude better than the lowest observed pressure during the experiment. The sintered pellet was heated to 400°C, and the 2.7 l. section between valve 1 and 2 was rapidly filled with CO_2 to a pressure of 9.7×10^{-4} Torr. The action of the getter caused the pressure to drop to 3.8×10^{-8} Torr in 20 min, as shown in Fig. 4.

This test procedure was repeated several times with the same getter pellet at different temperatures between 400 and 800°C. No attempt was made to degas the getter between runs, nor to pump down the test section. This action was justified by the fact that the getter has such sorbing capabilities that the gas sorbed for each previous run did not invalidate the subsequent test runs at higher temperatures. The getter pellet sorbed each additional gas injection at 400–800°C and the pressure dropped to about 5×10^{-8} Torr in 10 min. Under the same test conditions, still further gas injections were made at 900°C and 1000°C, respectively. The pressure dropped to approximately 2.5×10^{-7} Torr in 10 min (see Fig. 4).

The getter tests with CO_2 were culminated with the pellet at 400°C subjected to a continuous flow of gas at a constant pressure of 4×10^{-4} Torr. After 729 hr, there was no indication of any change in the gettering characteristics ; it may be assumed that the getter was not saturated.

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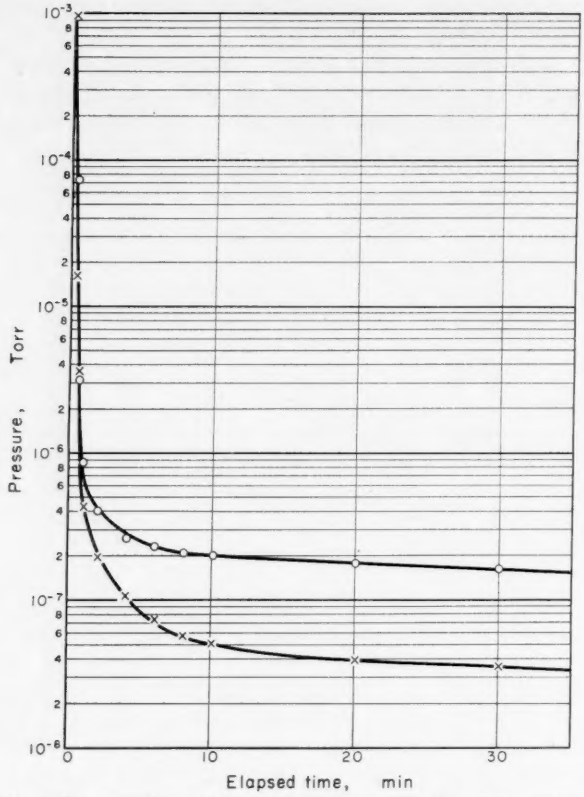

FIG. 4. The pumping action of the getter on CO_2 in a 2.7 l. system.
+, Average curve for 400–800 °C range.
○, Average curve for 900–1000 °C range.

Diffusion constant

The method used to determine the gettering characteristics of the CerAlloy 400 may be found in the cited references[1, 2]. The pertinent experimental data collected during this study may be clearly illustrated by the following graphical and tabular presentation. Figs. 5 and 6 are the curves used to calculate the partition coefficient and diffusion constant at 500 °C. These calculations were made by taking the zero time intercept of the relative pressure presentation and the slope of the relative pressure at long elapsed times. The original data from which Fig. 6 was constructed is shown in Fig. 5.

It is clearly evident from an examination of Figs. 5 and 6 that in obtaining the original data equilibrium pressure in the system had not been reached before the run was terminated. Therefore, some error is introduced in the data calculated and presented in Table I. These data are sufficiently close for the theoretical discussions and practical conclusions made in this paper. They are not, however, sufficiently accurate for extensive theoretical development, or for accurate prediction of the ultimate capabilities of the getter.

The calculated diffusion constants in Table I indicate an upward trend with temperature from 400 to 800 °C. Above this temperature, the diffusion constant decreases very rapidly with increasing temperature. One would expect

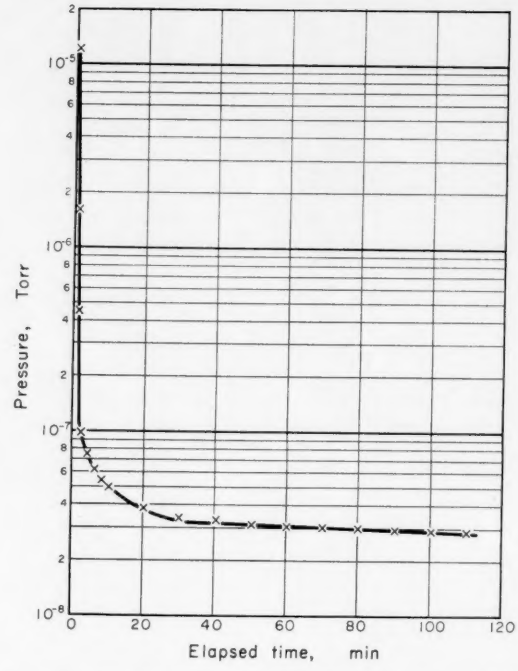

FIG. 5. The pumping action of the getter on CO_2 at 500 °C in a 2.7 l. system.

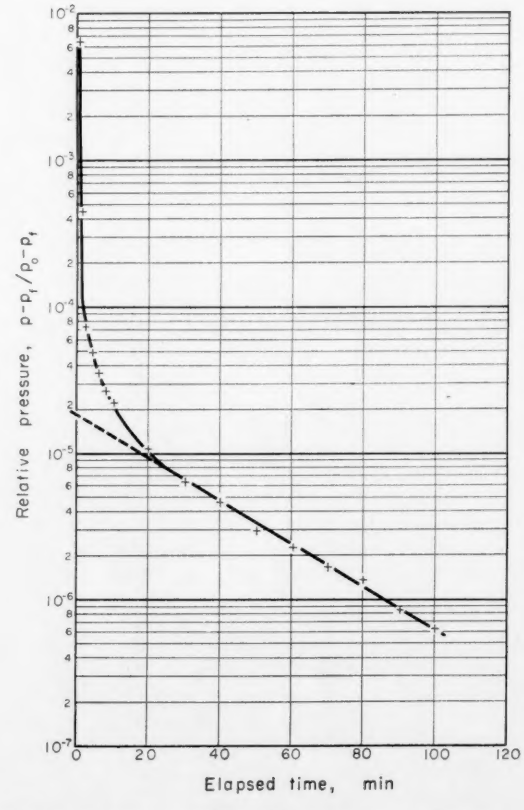

FIG. 6. Zero time extrapolation for the partition coefficient and the diffusion constant at 500 °C.

TABLE I

Diffusion constant and partition coefficient of CerAlloy 400 *with* CO_2

Temp. (°C)	Diffusion constant (cm^2/sec)	Partition coefficient
400	2.62×10^{-6}	8.35×10^{8}
500	2.92×10^{-6}	6.4×10^{8}
600	4.83×10^{-6}	6.74×10^{8}
700	2.74×10^{-6}	6.12×10^{8}
800	3.45×10^{-6}	8.96×10^{8}
900	8.7×10^{-7}	4.33×10^{8}
1000	2.15×10^{-7}	1.49×10^{8}

No probable error has been calculated because of the method used to record the data for the experiment.

that the diffusion constant would increase with temperature in a basically exponential fashion from the general conclusions of the classical diffusion theory. When the observed equilibrium pressure was plotted, see Fig. 7, it was noted that in the same 800–1000 °C range a rapid increase occurred. It is the purpose of this section to put forward an explanation for this correlation, and to attempt to relate it to the assumptions on which the theory is based.

With the first recognition of this temperature dependence inversion, it was felt that the calculated diffusion constant may be connected in some way with the observed equilibrium pressure which is known to be system-sensitive. This seemed a very likely possibility, since the background concentration of dissolved gas in the metal was assumed to be zero in the initial theoretical calculations. It is reasonable, however, to expect that the background concentration would be related in some way to the equilibrium pressure or the dissociation pressure of the chemical compounds formed.

In reference to Fig. 7, the equilibrium pressure follows the exponential function predicted by the theory at high temperature. As the temperature is lowered, the observed equilibrium pressure becomes comparable to the lowest pressure attainable in the particular system. Then as the getter lowers the pressure, as predicted by the theory, the outgassing of the system walls causes a steady state pressure instead of a true equilibrium pressure.

It is in the temperature range from 800 to 1000 °C that a correlation between the diffusion constant and the equilibrium pressure exists. It will be noted that the diffusion constant instead of increasing in the 800–1000 °C range decreases very rapidly. A plot shows this to be an exponential decrease. It is in this same temperature region that the equilibrium pressure increases exponentially. This suggests that the equilibrium pressure should be used as the true background concentration instead of zero in the theoretical calculation of the diffusion constant. This modification of the theory is, of course, important only in the extremely high temperature range. At the lower temperatures, the equilibrium pressure is so low that the assumed background concentration of zero is essentially valid.

In the data presented in Fig. 7, it is important to understand that the temperature at which the equilibrium pressure is a minimum is not necessarily the optimum gettering temperature because the equilibrium pressure is system-sensitive.

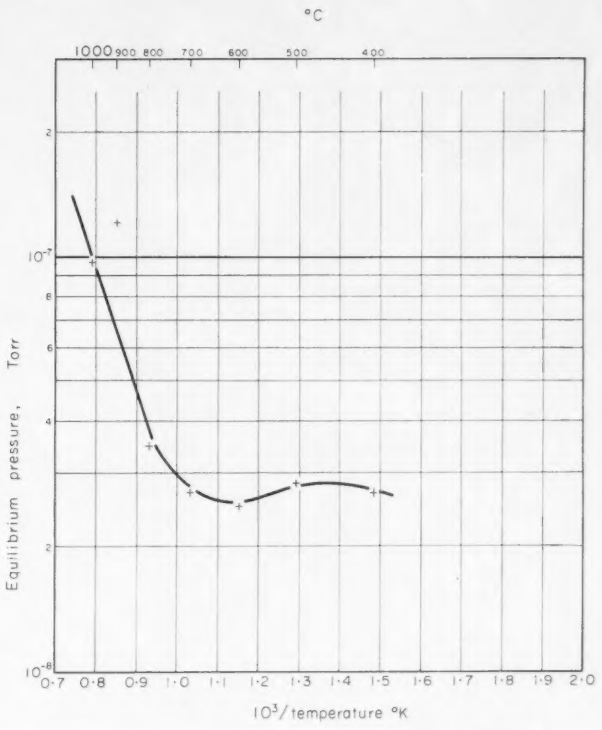

FIG. 7. Equilibrium pressure of CO_2 over CA 400 as a function of temperature.

Gettering rate

With use of the expression derived in the Appendix, the gettering rates were calculated as a function of time for all experimental temperatures between 400 and 1000 °C (see Table II).*

It appears probable from this tabular presentation that the gettering rate is dependent on pressure rather than time, since a subsequent test of 729 hr showed no change of getter characteristics. We must conclude, therefore, that the gettering rate is dependent upon pressure. To appreciate better this interdependence of gettering rate and pressure, consider the presentation in Fig. 8.

In Fig. 8 the gettering rate has been plotted as a function of temperature using time as a third variable. Apparently, the gettering rate reaches a maximum at temperatures between 500 and 600 °C and falls off sharply with further increases in temperature to 1000 °C. This high temperature behavior is probably closely associated with the theoretical limitations cited previously. Further consideration of this behavior will be delayed until the subject can be studied more fully. Below 800 °C the gettering rate appears to be relatively independent of temperature. There is, however, a marked decrease in the gettering rate as the gettering process proceeds and the pressure is lowered. This dependence is more clearly presented in Fig. 9 where the gettering rate of CA 400 for CO_2 is plotted as a function of pressure. It is interesting to note that at low pressures, the gettering rate is directly proportional to the pressure. At higher pressures, however, the gettering rate is limited and appears to approach an

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TABLE II

Gettering rate of CerAlloy 400 *with* CO_2 *in l/sec*

Time (sec)	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C	1000 °C
10	5.82×10^{-2}	6.35×10^{-2}	9.20×10^{-2}	6.04×10^{-2}	7.24×10^{-2}	2.18×10^{-2}	5.65×10^{-3}
30	4.05×10^{-2}	4.26×10^{-2}	4.33×10^{-2}	4.14×10^{-2}	4.37×10^{-2}	1.93×10^{-2}	5.45×10^{-3}
60	2.24×10^{-2}	2.22×10^{-2}	2.26×10^{-2}	2.16×10^{-2}	2.25×10^{-2}	1.61×10^{-2}	5.24×10^{-3}
120	1.17×10^{-2}	1.23×10^{-2}	1.32×10^{-2}	1.20×10^{-2}	1.23×10^{-2}	1.09×10^{-2}	4.79×10^{-3}
300	5.55×10^{-3}	5.17×10^{-3}	5.92×10^{-3}	5.67×10^{-3}	5.69×10^{-3}	4.66×10^{-3}	3.66×10^{-3}
600	3.11×10^{-3}	3.32×10^{-3}	3.85×10^{-3}	3.20×10^{-3}	3.65×10^{-3}	2.51×10^{-3}	2.29×10^{-3}

*The powdered CA 400 was shipped in acetone, which reacts with and probably alters the characteristics of this getter material. New lots are now shipped in hexane and so should yield even more favorable data.

asymptote at 10^{-1} l/sec as the pressure increases beyond 10^{-4} Torr. This behavior at higher pressures is in agreement with the assumptions made in the theoretical development for the gettering rate (see Appendix). The fact that the gettering rate does decrease at the lower pressures suggests modification of the theory.

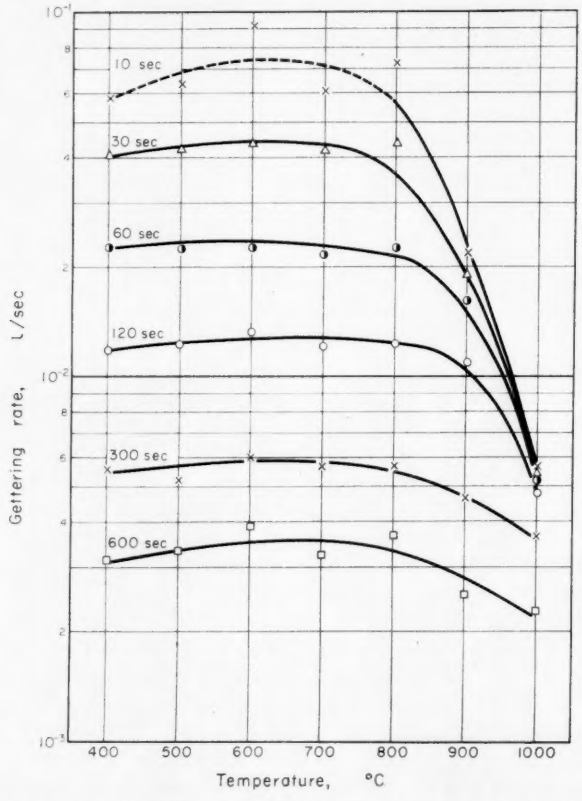

FIG. 8. Gettering rate as a function of temperature, using time as a third variable.

Conclusions

The diffusion constant and partition coefficient of carbon dioxide with CA 400 have been calculated as a function of temperature in this experimental study. The gettering rates have been calculated as a function of time, temperature, and pressure. In general, the theory presented by Doucette was found to be of value in the interpretation of the behavior of high temperature continuous getters. A detailed examination of the data, however, reveals that some modifications might be made in the theory to account for the background concentration of desorbed gas in the getter sample. Therefore, a correlation must be established between the background concentration in the gettering equation and the temperature dependent compound dissociation pressure. Furthermore, at low pressures it is necessary to modify the definition and form of the partition coefficient, in order to define equilibrium more appropriately. The equilibrium

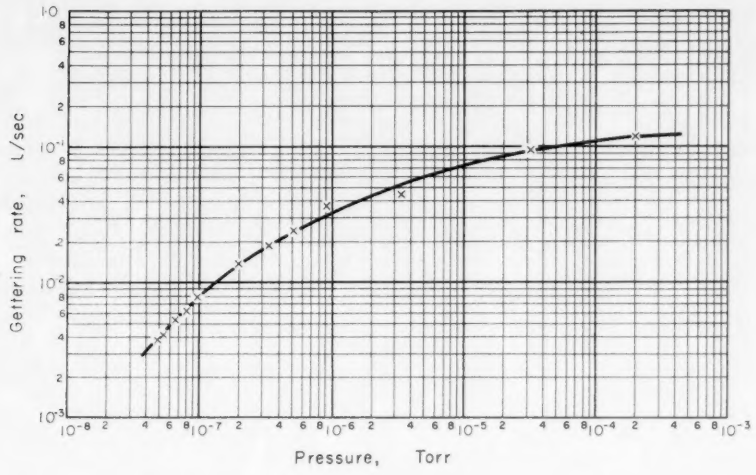

FIG. 9. Gettering rate as a function of pressure at 600°C.

definition should depend upon the relative energies of the two phases (gas and solid) which constitute the system. The partition coefficient may be determined by finding the sum of the occupation probability of each state over the range of all the states. Since the density of each state is not uniform with its energy, the partition coefficient must depend upon the level of occupation.

It has been demonstrated by this study, however, that CA 400 is an effective getter for carbon dioxide in the temperature range from 400 to 800°C. In most applications, the getter may be even used to 1000°C. The data indicate that CA 400 and similar alloys have considerable promise as getter materials in high ambient temperatures.

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Acknowledgement

The authors gratefully acknowledge their indebtedness to Dr. E. I. Doucette for his assistance in the preparation of this paper and for permission to quote some of his unpublished results.

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[3] P. della Porta and F. Ricca; "The Kinetics of the Adsorption of Nitrogen on Barium Getters," *Fifth National Symposium on Vacuum Technology Transactions*, p. 25. Pergamon Press, London (1959).
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APPENDIX

IN THIS appendix an expression will be derived for the adsorption rate of a continuous getter using the time dependent expression for pressure as previously derived by Doucette :

$$\frac{P - P_f}{P_0 - P_f} = \sum_{n=1}^{\infty} f(S,q_n) \exp[-q_n^2 Dt/r_0^2] \tag{A1}$$

where

$$f(S,q_n) = \frac{6S(1-S)}{9(1-S)-S^2q_n^2}. \tag{A2}$$

The rate at which the pressure decreases with time may be derived by taking the first time derivative of the pressure

$$\frac{dP}{dt} = (P_0 - P_f) \sum_{n=1}^{\infty} \frac{q_n^2 D}{r_0^2} f(S,q) \exp[-q_n^2 Dt/r_0^2]. \tag{A3}$$

Using the conventional definition of gettering rate, $\mathcal{S}$,

$$\mathcal{S} = -\frac{V}{P}\frac{dP}{dt} \tag{A4}$$

the gettering rate becomes

$$\mathcal{S} = V \frac{\sum_{n=1}^{\infty} \frac{q_n^2 D}{r_0^2} f(S,q) \exp[-q_n^2 Dt/r_0^2]}{\sum_{n=1}^{\infty} f(S,q) \exp[-q_n^2 Dt/r_0^2] + \frac{P_f}{P_0 - P_f}}. \tag{A5}$$

Considering the present state of experimental developments, one finds it unnecessary to use equation (A5) in its entirety. It is possible to make some simplifying assumptions with regard to the magnitudes of the partition coefficient to simplify the equation considerably, and to expedite calculation. Since the value of S is always very small compared with q or with unity, equation (A2) may be simplified to the form

$$f_1(S,q_n) = \frac{2S}{3} \tag{A6}$$

when $$S^2q_n^2 << 9(1-S).$$

Inserting f_1 for f in equation (5) results in

$$\mathcal{S} = \frac{VD \sum_{n=1}^{\infty} q_n^2 \exp[-q_n^2 Dt/r_0^2]}{r_0^2 \sum_{n=1}^{\infty} \exp[-q_n^2 Dt/r_0^2]}. \tag{A7}$$

It has also been assumed here that $\frac{P_f}{P_0 - P_f}$ is very small and may be neglected.

Reibungsvakuummeter "REVA" *

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Es wird ein neues für die Verwendung in der Praxis bestimmtes Vakuummeter mit einem Messbereich von 760 zu 10^{-3} Torr beschrieben. Das Arbeitsprinzip beruht auf der mit dem Gasdruck veränderlichen Reibung eines schwingenden, metallischen Bändchens. Der Strom, der dazu erforderlich ist, die Amplitude des schwingenden Bändchens konstant zu halten, ist ein Mass für die Reibung, die überwunden werden muss, und somit ein Mass für den herrschenden Gasdruck. Der Vorteil dieser Anordnung besteht darin, dass das Messergebnis nicht durch die innere Dämpfung beeinträchtigt wird, weil diese infolge der konstanten Amplitude über den gesamten Messbereich konstant bleibt. Es wird der elektronische Aufbau des Verstärkers mit den Sondermassnahmen zur Kompensation der inneren Reibung des Bändchens und der Regeleinrichtung zur Konstanthaltung der Amplitude beschrieben. Ferner werden Abbildungen des Messorgans und des kompletten Gerätes gezeigt. Auf die Abhängigkeit der Anzeige von der Gasart wird näher eingegangen. Im Gebiet von Drücken, die kleiner als 10^{-1} Torr sind, ist die Anzeige der Wurzel aus dem Molekulargewicht proportional. Oberhalb von 10^{-1} Torr liegt keine eindeutige Gesetzmässigkeit mehr vor und man kann nicht durch einfache Multiplikation für eine andere Gasart umrechnen. Eine besondere Eichung für eine andere Gasart ist dann erforderlich.

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"REVA" Friction Vacuum Gauge†

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A new vacuum gauge, with a measuring range from 760 to 10^{-3} Torr for practical use is described here. The working principle is based on the friction, dependent on gas pressure, of an oscillating metal ribbon. The current required for keeping the amplitude of the vibrating ribbon constant is a measure of the friction which must be overcome and thus also a measure of the prevailing gas pressure. The advantage of this arrangement lies in the fact that the measurements are not adversely affected by internal damping, because it remains constant on account of the constant amplitude along the entire measuring range. The electronic design of the amplifier together with the special measures taken for compensating the internal friction of the ribbon and the control equipment for keeping the amplitude constant are then described. Details are given concerning the dependence of the reading upon the kind of gas. Illustrations of the measuring element and the complete equipment are also shown. Within the pressure ranges below 10^{-1} Torr, the reading is proportional to the root of the molecular weight. Above 10^{-1} Torr, there are no specific control laws, and conversions cannot be made simply by multiplying for another type of gas. Special calibration for another kind of gas must then be made.

*Nach einem Vortrag anlässlich der "Internen Fachsitzung der Arbeitsgemeinschaft VAKUUM", am 26 Oktober 1959 im Institut für angewandte Physik der Universität Mainz.

†According to a lecture given at the "Interne Fachsitzung der Arbeitsgemeinschaft VAKUUM," on 26 October 1959, in the Institute for Applied Physics of the University Mainz.

Allgemeines

Vakuummeter, bei denen die Reibung eines schwingenden Körpers mit den umgebenden Gasen als Massstab für den Druck verwandt wurde, sind schon lange bekannt. Bei den ersten Ausführungen benutzte man ein schwingungsfähiges System, meistens einen Quarzfaden, der einseitig eingespannt war und regte diesen durch einen einmaligen Impuls an. Je nachdem der Druck niedriger oder höher war, ergab sich dabei eine mehr oder weniger lange Ausschwingzeit. Diese Zeit wurde als Mass für den Druck angewendet. Die Vakuummeter hatten den Nachteil, dass bei gutem Vakuum sehr lange Ablesezeiten auftraten, eine kontinuierliche Anzeige nicht erfolgen konnte, und dass sie ausserdem sehr erschütterungsempfindlich waren. Ein kleiner Stoss genügte, um die eingeleitete Messung zunichte zu machen.

Klumb und Schwarz bauten erstmals ein Reibungsvakuummeter mit kontinuierlicher Anzeige*. Hierbei wurde ein schwingungsfähiges System über einen Verstärker in seiner Eigenfrequenz angeregt und die Amplitude der Schwingung gemessen. Die Erregung wurde hierbei konstant gehalten. Die Amplitude der Schwingung wurde über einen Spiegel zur Anzeige gebracht.

Nachteilig an diesem Gerät war der Umstand, dass die Anzeige an den Ort des Messsystems gebunden war, sodass eine Fernablesung, z.B. an einer Schalttafel, nicht ohne weiteres möglich war. Ausserdem hat das Prinzip der konstanten Erregung einen wesentlichen Mangel. Im Bereich der kleinen Drücke wird die Reibung mit den Restgasen mit fallendem Druck geringer. Dadurch nimmt die Amplitude zu, bis sich ein Gleichgewicht zwischen anregender Energie und Dämpfung ausbildet. Mit zunehmender Amplitude nimmt aber die innere Dämpfung des Systems ebenfalls zu, sodass bei niedrigen Drücken der durch die Reibung hervorgerufene Anteil der äusseren Dämpfung im Verhältnis zur Gesamtdämpfung kleiner wird. Die Messgenauigkeit wird mit sinkendem Druck immer geringer, weil dann die innere Dämpfung des Systems als störender Wert im Verhältnis zu der Reibung, die man messen will, sehr gross ist.

Prinzip

Angeregt durch die Arbeiten von Klumb und Schwarz haben wir uns mit dem Reibungsvakuummeter befasst und versucht, die geschilderten Mängel zu beseitigen, um ein für die Praxis brauchbares Gerät zu schaffen.

Als schwingendes System benutzen wir ein in einem Magnetfeld ausgespanntes Band aus einem hochelastischen Metall. Das Prinzip ist in Abb. 1 dargestellt. Im Röhrenkörper (1) befindet sich der Permanentmagnet (2) mit dem ausgespannten Messband (3). Schwingt das Band im Magnetfeld, so entsteht eine elektrische Wechselspannung. Diese wird einem Verstärker (4) zugeführt, der einen Ausgangsstrom liefert, welcher seinerseits wieder das Band in seiner Eigenfrequenz zum Schwingen anregt. Dabei ist der Verstärker so ausgeführt, dass die Amplitude des schwingenden Bandes konstant gehalten wird. Der zur Erregung erforderliche Strom wird von dem Instrument (5) angezeigt.

*ATM V 1341, Lieferung 194, März 1952.

General observations

Vacuum gauges in which the friction of a vibrating body with the surrounding gases is used to measure the existing pressure, have already been known for a long time. In the first models, a system capable of vibration was used, usually a quartz fibre fastened at one end which was excited by a single impulse. A longer or shorter oscillation period resulted depending upon whether the pressure was lower or higher. This period was used as a measure of the prevailing pressure. These vacuum gauges had the disadvantages that very long reading periods resulted in a good vacuum, that a continuous indication could not be obtained and that they were extremely sensitive to shock and vibration. A slight impact was enough to render the measurement in progress useless.

Klumb and Schwarz designed and constructed the first friction vacuum gauge with continuous indication*. For this, a system capable of vibration was excited over an amplifier in its inherent frequency and the amplitude of oscillation was measured. The impulses were kept constant, and the amplitude of the oscillations were shown through a mirror.

With this apparatus, indication was limited to the location of the measuring system, a great disadvantage since remote indication and reading, e.g. at a control panel, were not easily possible. The principle of constant impulses also has a great drawback. In the low pressure range, friction with the residual gases decreases with decreasing pressure. This means that the amplitude increases until it reaches an equilibrium between the stimulative energy and damping. However, with a rising amplitude, internal damping of the system also increases, so that with low pressures the external damping caused by friction becomes lower in proportion to the overall damping. With decreasing pressure, the measuring accuracy also steadily decreases since the internal damping of the system is a very highly disturbing value in proportion to the friction intended to be measured.

Measuring principle

Inspired by the work of Klumb and Schwarz, we have studied the friction vacuum gauge and tried to remove existing deficiencies in order to create and design a completely practical instrument.

As an oscillating system, we used a ribbon made of highly-flexible metal, stretched across a magnetic field. This principle is shown in Fig. 1. The tube body (1) contains the permanent magnet (2) with the stretched measuring ribbon (3). When the ribbon oscillates within the magnetic field, an electric alternating voltage results. This voltage is fed to an amplifier (4) which supplies the output current which, in turn, excites the ribbon in its inherent frequency. The amplifier is thus so designed that the amplitude of the oscillating ribbon remains constant. The current necessary is shown by the instrument (5). It is in proportion to the

*ATM V 1341. Delivery 194, March 1952.

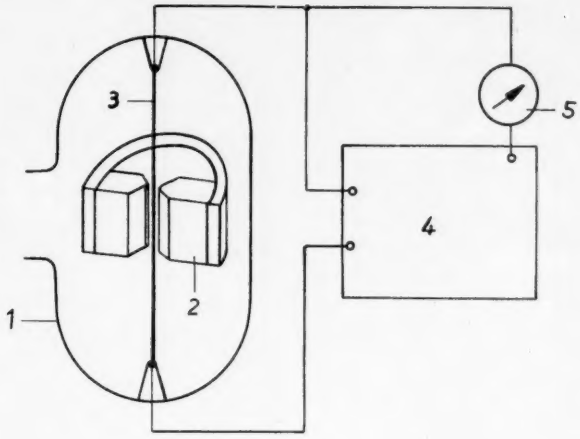

Abb. 1. Schematische Anordnung. Es bedeuten: 1 = Messröhre, 2 = Permanentmagnet, 3 = Metallband, 4 = Verstärker, 5 = Anzeige-Instrument.

Fig. 1. Circuit diagram. 1 = measuring tube; 2 = permanent magnet; 3 = metal ribbon; 4 = amplifier; 5 = indicating instrument.

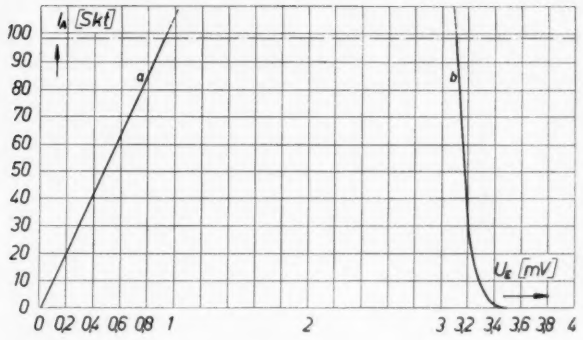

Abb. 2. Verstärker—Kennlinie. Ausgangsstrom I_A als Funktion der Eingangsspannung U_E.

Fig. 2. Amplifier—characteristic curve. Output current I_A as function of the input voltage U_E.

Er ist der Dämpfung des schwingenden Bandes proportional und somit ein Mass für den Druck.

Um zu erreichen, dass das im Magnetfeld ausgespannte Band mit nahezu konstanter Amplitude schwingt und der Erregerstrom sich auf den jeweils erforderlichen Wert einstellt, muss der Verstärker die in Abb. 2 dargestellte Charakteristik aufweisen. Auf der Abszisse ist die Eingangsspannung des Verstärkers und auf der Ordinate der Ausgangsstrom aufgetragen. Die Kurve beginnt im Nullpunkt mit dem Einschalten des Gerätes. Im Kurvenast (a) steigt der Ausgangsstrom proportional zur Eingangsspannung. Der Verstärkungsgrad ist so gewählt, dass im Anfang der Ausgangsstrom auch bei Atmosphärendruck wesentlich grösser ist als der zur Aufrechterhaltung der Amplitude erforderliche Wert. Dadurch wird das Band zur Schwingung in seiner Eigenfrequenz angeregt. Nach kurzer Einschwingzeit und dabei zunehmender Eingangsspannung des Verstärkers muss sich dann der Ausgangsstrom entsprechend Kurvenast (b) so weit verringern, bis sich der Gleichgewichtszustand zwischen der zugeführten Energie und der Dämpfung des schwingenden Bandes einstellt.

Die Dämpfung des Bandes setzt sich, wie schon erwähnt, aus der inneren und der äusseren Reibung zusammen. Die äussere Reibung ist abhängig vom Druck der umgebenden Gase, die innere Reibung ist abhängig vom Material. Die innere Reibung soll über dan ganzen Messbereich einen konstanten Wert behalten. Um dies zu erreichen, ist es

damping of the oscillating ribbon and thus is a measure of the prevailing pressure.

In order to ensure that the ribbon stretched across the magnetic field oscillates almost constantly and that the energizing current will always adjust itself to the required value, the amplifier must have the characteristic properties shown in Fig. 2. The input voltage of the amplifier is plotted on the abscissa, and the output current on the ordinate. The curve starts at the zero point when the instrument is turned on. In the curve branch (a), the output current rises proportionally with the input voltage. The degree of amplification is selected so that at the beginning the output current is also considerably higher at atmospheric pressure than the value necessary to retain the amplitude. For this reason, the ribbon vibrates because of impulses in its inherent frequency. After a short transition period, and a simultaneously increasing input voltage by the amplifier, the output current must decrease, corresponding to the curve branch (b) until equilibrium is attained between the energy supplied and the damping of the oscillating ribbon.

As mentioned above, the damping of the ribbon is composed of the internal and external friction. The external friction depends upon the pressure of the surrounding gases, while the internal friction depends upon the material used. The internal friction should remain constant through the entire measuring range. In order to achieve this, it is

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unbedingt erforderlich, die Amplitude konstant zu halten, weil die innere Reibung nicht linear von der Amplitude abhängig ist. Dies sei am Beispiel des Verhaltens von Stahl erläutert : In dem Buch *Technische Physik der Werkstoffe* gibt Zwicker eine Kurve über den Verlustwinkel von Stahl bei hohen Belastungen an. Abb. 3 zeigt diese Kurve, in der der Verlustwinkel bei steigender Belastung erst langsam zunimmt und dann später sehr steil ansteigt.

Arbeitet man bei einem Vakuummeter mit variabler Amplitude, so können ganz erhebliche Fehler durch die Zunahme der inneren Reibung entstehen. Arbeitet man dahingegen mit konstanter Amplitude, so kann man im Bereich kleiner innerer Dämpfung bleiben und kann diese, da die konstant ist, elektrisch kompensieren, so dass das Vakuummeter in seinem Endbereich auf 0 geht und nicht einen Restbetrag anzeigt, der von der inneren Reibung herrührt. Unter Berücksichtigung dieser grundlegenden Forderung wurde das Reibungsvakuummeter " REVA ", wie in folgendem geschildert, praktisch ausgeführt.

absolutely necessary to keep the amplitude constant because the internal friction is not lineary dependent upon the amplitude. This can be described as an example on the behaviour of steel : In the book entitled *Technische Physik der Werkstoffe*, the author, Zwikker, illustrates a curve concerning the phase angle (loss angle) of steel at high loads. Fig. 3 shows this curve in which the phase angle first increases slowly and later rises very steeply.

If a vacuum gauge was used with a variable amplitude, extremely high errors could be caused by the increase of internal friction. If, on the other hand, operation could be carried out with a constant amplitude, there would be a smaller range of internal damping and it would be possible—because it is constant—to compensate this damping electrically so that the vacuum gauge would return ultimately to zero and would not indicate a residual value caused by internal friction. Taking into consideration this basic demand, the friction vacuum gauge, " REVA ", has been practically designed in the manner described below :

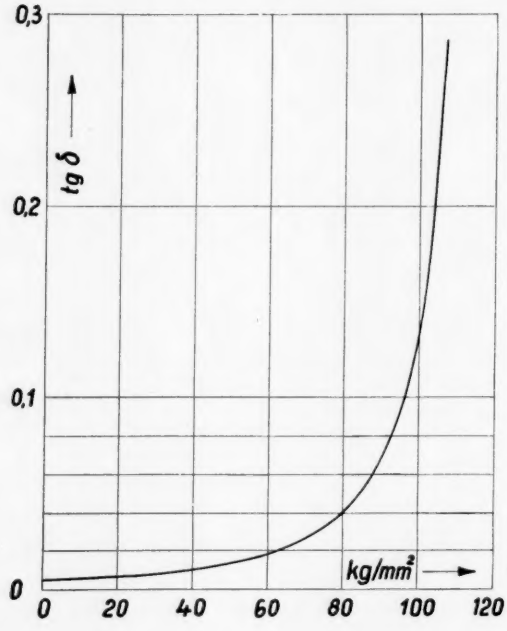

ABB. 3. Verlustwinkel tgδ von Stahl in Abhängigkeit von der Belastung.

FIG. 3. Phase angle (loss angle) tgδ of steel dependent upon the load.

Praktische Ausführung

Die Abb. 4 zeigt den Aufbau des Messsystems. In der Mitte erkennt man den Permanentmagneten, in dessen Luftspalt ein Metallband ausgespannt ist. Mit den beiden Kreuzlochschrauben kann man das Band spannen und die günstigste Frequenz einstellen.

Das Messsystem ist mit acht Federn in einem Rahmen aufgehängt. Dieser Rahmen ist fest mit dem Röhrenkörper verbunden. Die Eigenfrequenz der Aufhängung liegt bei etwa 20 Hz., während das Band selbst mit etwa 225 Hz. schwingt. Durch diese Anordnung werden Störschwingungen von aussen ferngehalten. Selbst leichte Hammerschläge auf die Röhre beeinflussen die Messung nicht. Am Eingang der Röhre befindet sich noch ein Fangmagnet, der mag-

Practical design and construction

Fig. 4 shows the design and construction of the measuring system. In the centre, the permanent magnet can be seen through the air gap of which a metal ribbon is stretched. The ribbon can be stretched by the two capstan head screws and so adjusted to the most suitable frequency.

The measuring system is suspended within a frame by means of eight springs. This frame is firmly connected with the body of the tube. The inherent frequency of the suspension lies at about 20 c/s, while the ribbon itself oscillates at about 225 c/s. This arrangement excludes interfering oscillations from outside. Even slight hammer blows on the tube do not affect the measurement. A collecting magnet is fitted to the inlet of the tube and retains magnetic chips

netische Späne von dem Messsystem fernhält. Es könnte sonst der Fall eintreten, dass ein magnetischer Span in den Luftspalt gezogen wird und dadurch das Messband behindert.

Abb. 5 zeigt das Schaltbild des Verstärkers. Das Messband ist direkt an einen Eingangsübertrager angeschlossen, um eine möglichst hohe Eingangsspannung an der ersten Verstärkerröhre zu erhalten. Die Amplitude des Messbandes beträgt etwa 0,1 mm. Bei dieser kleinen Amplitude entsteht

from the measuring system. Otherwise, it might be possible for a magnetic chip to be drawn into the air gap and obstruct the measuring ribbon.

Fig. 5 shows the circuit diagram of the amplifier. The measuring ribbon is connected directly to an input transmitter in order to obtain the highest possible input voltage at the first amplifier tube. The amplitude of the measuring ribbon amounts to about 0.1 mm. With this low amplitude,

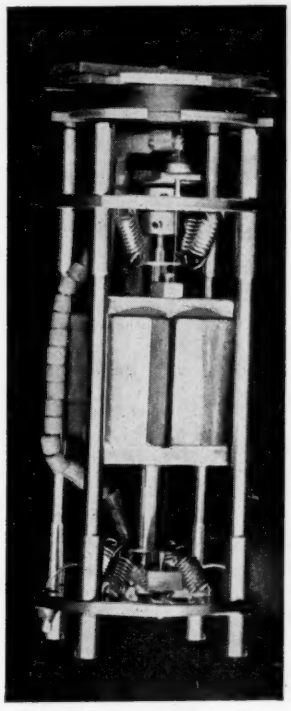

Abb. 4. Messsystem.

Fig. 4. Measuring system.

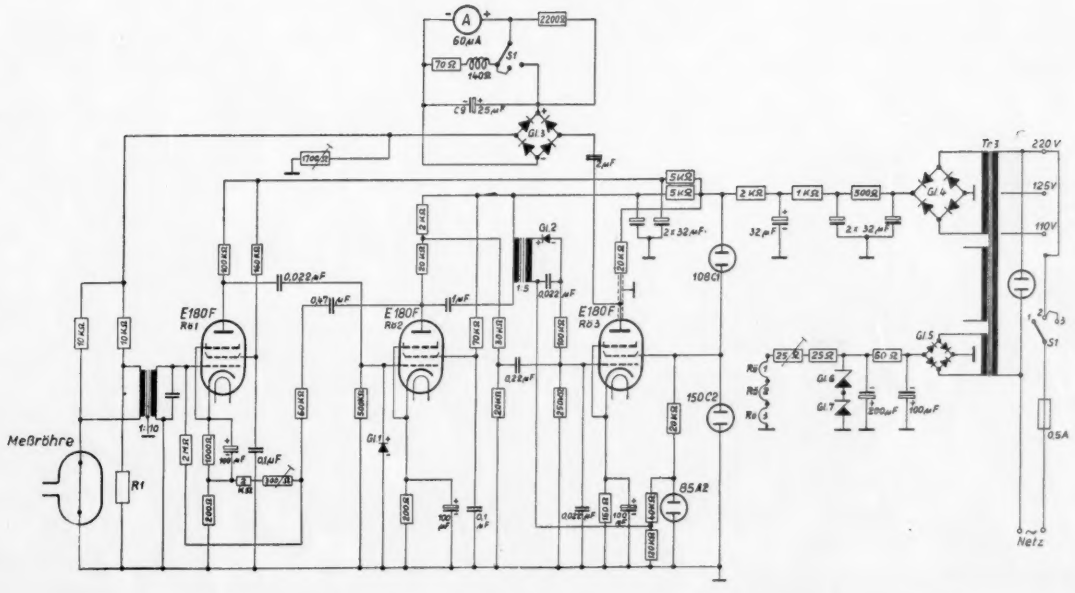

Abb. 5. Schaltbild.

Fig. 5. Circuit diagram.

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eine Spannung von 3 mV, die durch den Eingangsübertrager auf 30 mV erhöht wird. In zwei Verstärkerstufen, die stark gegengekoppelt sind, wird die Spannung auf 60 V verstärkt. Diese Spannung wird gleichgerichtet und geglättet. Eine stabilisierte Gleichspannung wird dieser Spannung entgegengeschaltet und die Differenz der beiden Spannungen als Regelspannung einer dritten Verstärkerröhre zugeführt. Wenn also beispielsweise die Wechselspannung von 60 V auf 58 V abfällt, so steht eine Regelspannung von +2 V zur Verfügung. Steigt dagegen die Wechselspannung auf 62 V, so steht eine Regelspannung von −2 V zur Verfügung. In letzterem Grenzfall ist die dritte Verstärkerröhre, die als Regelstufe dient, schon so weit zurückgeregelt, dass nur noch ein ganz geringer Ausgangsstrom fliesst. Ausser der Regelspannung wird dem Steuergitter der dritten Verstärkerröhre auch die Wechselspannung zugeführt. Der Ausgangsstrom der dritten Röhre, der damit amplitudenabhängig geregelt ist, wird über einen Gleichrichter, der das Mikro-Ampèremeter speist, der Messröhre zugeführt.

Um den Ohmschen Spannungsabfall in dem Messband zu kompensieren, wurde eine Brückenschaltung gewählt, so dass dem Übertrager nur die durch die Schwingung erzeugte EMK zugeführt wird, aber nicht der durch den Widerstand bedingte Spannungsabfall. Der der Brücke zugeführte und vom Instrument angezeigte Strom ist demnach doppelt so gross wie der, der zur Aufrechterhaltung der Amplitude des Messbandes erforderlich ist.

Bei der Verwendung eines Übertragers am Eingang entstehen elektrische Verluste, die sich zu den Verlusten der inneren Reibung addieren. Um diese Verluste auszugleichen, wird der zweiten Verstärkerstufe eine Teilspannung entnommen und dem Gitter der ersten Röhre zugeführt. Diese Teilspannung ist so gewählt, dass gerade die mechanische Dämpfung des Messbandes und die elektrische Dämpfung des Übertragers ausgeglichen werden. Diese Rückkoppelung zur Kompensation der Dämpfung bringt aber noch einen zweiten Vorteil mit sich. Wenn beispielsweise keine Röhre an das Gerät angeschlossen ist, so können kapazitive Störeinflüsse auf den Eingang des Übertragers, der verhältnismässig hochohmig ist, einwirken. Dies hätte zur Folge, dass das Messinstrument einen gewissen Ausschlag anzeigt. Man könnte dann an dem Instrument nicht erkennen, ob ein bestimmtes Vakuum vorliegt order keine Röhre in Betrieb ist. Dem Eingangsübertrager ist daher ein Kondensator parallel geschaltet, der mit dem Eingangsübertrager zusammen einen Schwingkreis bildet. Durch den Wegfall der mechanischen Dämpfung der Röhre wird dieser Schwingkreis durch die Rückkoppelung zum Schwingen angeregt. Es baut sich eine grosse Amplitude auf, die eine so grosse Regelspannung zur Folge hat, dass die Endröhre vollkommen gesperrt wird. Durch diese Massnahme wird das Anzeigeinstrument stromlos, wenn das Gerät in Betrieb, aber keine Röhre angeschlossen ist. Bei angeschlossener Röhre ist der Schwingkreis gegenüber der Röhre so hochohmig, dass die Frequenz des Messbandes bestimmend ist und den Verstärker einwandfrei steuert.

Der Zeigerausschlag, der sich in Abhängigkeit vom Druck für die bisher beschriebene Ausführung des Gerätes ergibt, ist in Abb. 6 als Kurve (1) dargestellt. Damit man im

a voltage of about 3 mV is obtained which is increased to 30 mV by the input transmitter. In two amplification stages, with a highly inverse feedback, this voltage is increased to 60 mV. This voltage is rectified and smoothed. A stabilized direct current voltage is counter-connected to this voltage and the difference between the two voltages is fed to a third amplifier tube in the form of control potential. If, for example, the alternating voltage of 60 V drops to 58 V, a control potential of +2 V is available. If, on the other hand, the alternating voltage rises to 62 V, a control potential of −2 V is also available. In the latter case, the third amplifier tube, which serves as control stage, is already adjusted so far in reverse that only a very insignificant amount of output current flows. Apart from the control voltage, the alternating voltage is also fed to the control grid of the third amplifier tube. The output current of the third tube, controlled according to the amplitude, is fed to the measuring tube over a rectifier which feeds the micro-ammeter.

In order to compensate the ohmic voltage drop, a bridge circuit has been chosen so that only the e.m.f. produced by the oscillation is fed to the transmitter, and not to the voltage drop caused by the resistance. The current fed to the bridge and indicated by the instrument is double the power of that required to maintain the amplitude of the measuring ribbon.

When using a transmitter at the input of the instrument, electrical losses occur which add to the losses caused by internal friction. In order to balance these losses, partial voltage is taken from the second amplifier stage and fed to the grid of the first amplifier tube. This partial voltage is selected so that the mechanical damping of the measuring ribbon and the electric damping of the transmitter are just balanced. The feedback to compensate the damping, however, has also a second advantage. If, for instance, no tube is connected with the instrument, influences disturbing the capacity could affect the input of the transmitter which is comparatively highly ohmic. This would, in turn, result in some indication on the measuring instrument. In this case, one could not ascertain from this instrument whether there is a certain vacuum or whether the tubes are not operating.

For this reason, a condenser is connected in parallel to the input transmitter and, together with the input transmitter, it forms an oscillatory circuit. Due to the omission of the mechanical damping of the tube, this oscillatory circuit vibrates by means of the feedback. A high amplitude is thus formed, resulting in such a high control voltage that the final tube is completely cut off. This means that the indicator becomes de-energized if the instrument is operating without any tube being connected. When the tubes are connected, the oscillatory circuit is so highly ohmic compared to the tube that the frequency of the measuring ribbon is the determining factor and controls the amplifier perfectly.

The pointer deflection which depends upon the pressure on the instrument described so far, is shown as curve (1) in Fig. 6. In order to be able to recognize the curve better

Bereich niedriger Drücke den Verlauf besser erkennen kann, ist die Kurve (2) für den kleinen Messbereich im Verhältnis 1 : 10 vergrössert aufgetragen. Im Bereich von 10^{-3} bis 10^{-1} Torr sind der Druck und der Zeigerausschlag einander proportional. Oberhalb von 10^{-1} Torr nimmt der Zeigerausschlag bei steigendem Druck in geringerem Masse zu. Es ergibt sich etwa eine logarithmische Charakteristik. Am unempfindlichsten ist das Gerät im Bereich zwischen 10 und 100 Torr, während es oberhalb von 100 Torr wieder stärker anspricht. Die sich dabei ergebende Skala ist nicht ideal. Im interessantesten Bereich zwischen 10^{-2} und 10 Torr ist sie zu stark zusammengedrückt, während der Bereich von 100 Torr bis Atmosphärendruck einen recht grossen Raum einnimmt. Dieses Gebiet ist aber im allgemeinen nicht so interessant, weil man hier im praktischen Betrieb von dem Gerät nicht so grosse Genauigkeit verlangt. Für genauere Angaben in diesem Bereich gibt es einfachere und billigere Vakuummeter. Um die Anzeige in diesem Sinn günstiger zu gestalten, wurde der Messbereich zwischen 100 Torr und Atmosphärendruck durch eine besondere Massnahme zusammengedrückt und gleichzeitig durch Erhöhung der Empfindlichkeit des Anzeigeinstrumentes der Bereich niedriger Drücke auseinandergezogen.

Wir haben dies in einfacher Weise dadurch erreicht, dass der Widerstand R^1 im Brückenzweig, der zur Kompensation des Innenwiderstandes des Messbandes vorgesehen ist, etwas niedriger gewählt wurde. Dadurch wurde die Amplitude des Messbandes und damit der Zeigerausschlag im Bereich höheren Druckes verringert.

Im Gebiet niedriger Drücke wirkt sich diese Massnahme nicht aus, weil dort die Ströme noch klein sind, so dass man den Spannungsabfall durch den Ohmschen Widerstand vernachlässigen kann. Im Gebiet der hohen Drücke, insbesondere bei Atmosphärendruck, hat der Spannungsabfall schon einen wesentlichen Einfluss und man erreicht also, dass im Gebiet hoher Drücke der Messbereich zusammengedrückt wird. Die Kurve (2) der Abb. 6 stellt den Verlauf dar, wie er sich nach Verringerung der Amplitude ergibt. Die Kurve (2), ist aber durch Vergrösserung der Empfindlichkeit des Messinstrumentes über den ganzen Messbereich auseinandergezogen. Wie man sieht, ist die

in the lower range of pressures, curve (2) for the low measuring range is plotted enlarged, to the scale 1 : 10. Within a range 10^{-3}–10^{-1} Torr, the pointer deflection increases slightly with rising pressure. Thus, an approximately logarithmical characteristic curve results. The instrument is least sensitive between 10 and 100 Torr, while it reacts more strongly in the range above 100 Torr. The resulting scale is not ideal. In the most interesting range between 10^{-2} and 10 Torr, it is too compressed, while the range from 100 Torr up to atmospheric pressure is extended. This range, however, is not usually very interesting because, in practice, accuracy to this degree is not demanded from the instrument. There are far more simple and less expensive vacuum gauges available for this range. In order to show the indication more favourably in this respect, the measuring range between 100 Torr and atmospheric pressure has been compressed by special measures and, at the same time, the range of lower pressures has been widened by increasing the sensitivity of the measuring instrument.

We have achieved this in a simple manner by selecting a somewhat lower resistance R_1 in the bridge branch which is provided in order to compensate the inherent resistance of the measuring ribbon. In this way, the amplitude of the measuring ribbon and the pointer deflection in the range of higher pressures were both decreased.

Within the lower pressures range, this measure has no effect because the currents are still low so that the voltage drop caused by the ohmic resistance can be neglected. In the range of high pressures, especially at atmospheric pressure, the voltage drop has already a considerable influence and so in the range of high pressure, the measuring range is compressed. Curve (2) of Fig. 6 shows the curve resulting after decreasing the amplitude. Curve (3) corresponds with curve (2), but is extended over the entire measuring range by increasing the sensitivity of the measuring instrument.

As can be seen, compared to curve (1), curve (3) is more satisfactory because the range of lower pressures is widened while that of the high pressures is compressed.

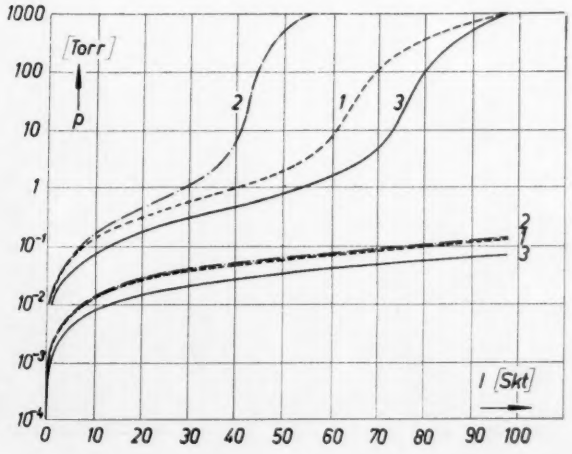

Abb. 6. Zeigerausschlag in Abhängigkeit vom Druck.
Kurve 1 bei völlig konstanter Amplitude ;
Kurve 2 mit bei hohen Drücken reduzierter Amplitude ;
Kurve 3 entspricht Kurve 2, jedoch auseinandergezogen.

Fig. 6. Pointer deflection dependent upon the pressure.
Curve 1, at completely constant amplitude ;
Curve 2, with reduced amplitude at high pressures ;
Curve 3, corresponds to Curve 2, but extended.

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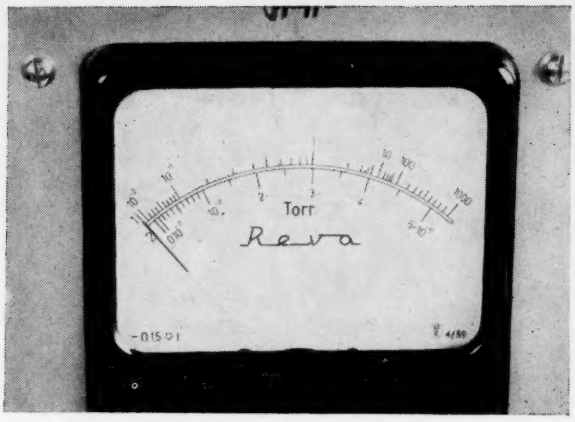

ABB. 7 (*rechts*). Skala des Messgerätes " REVA ".

FIG. 7 (*right*). Scale of the measuring instrument " REVA ".

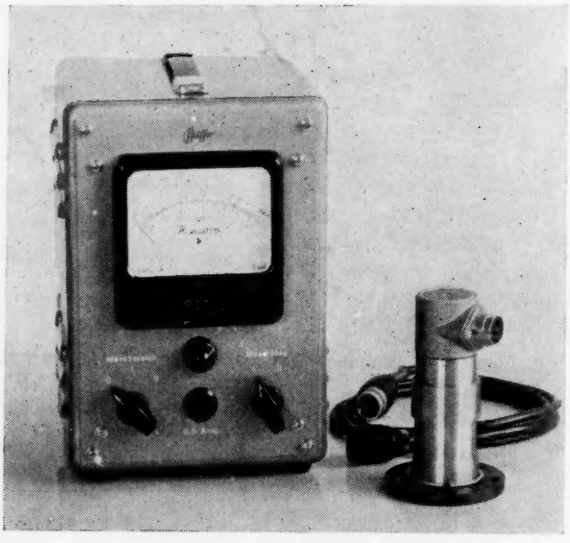

ABB. 8 (*links*). Gesamtansicht des Messgerätes " REVA ".

FIG. 8 (*left*). Overall view of the " REVA " friction vacuum gauge.

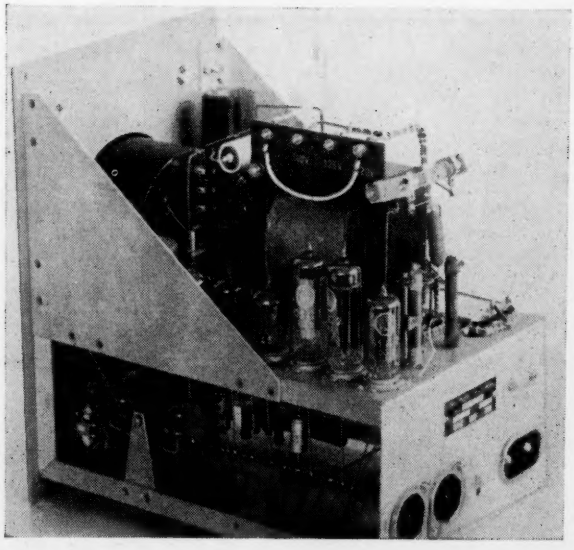

ABB. 9 (*rechts*). Innenansicht des Verstärkers.

FIG. 9 (*right*). Interior view.

Kurve (3) gegenüber der Kurve (1) vorteilhafter, weil das Gebiet niedriger Drücke auseinandergezogen und das Gebiet hoher Drücke zusammengedrängt ist.

Abb. 7 zeigt die Skala, die dieser Ausführung entspricht. Der gesamte Messbereich ist in zwei Bereiche unterteilt: 10^{-2} Torr bis 1000 Torr und 10^{-3} bis 10^{-2} Torr. Die Umschaltung auf die beiden Teile der Skala erfolgt durch einen Messbereichsschalter. Abb. 8 zeigt eine Ansicht des so ausgeführten Gerätes mit Messröhre und Abb. 9 den inneren Aufbau.

Abhängigkeit von der Gasart

Theoretisch müsste, bei anderen Gasen als bei Luft, der Zeigerausschlag der Wurzel aus dem Molekulargewicht proportional sein. Eine solche Abhängigkeit zeigt sich auch im Gebiet niedriger Drücke. Abb. 10 zeigt die Eichkurven für verschiedene Gase im Gebiet niedriger Drücke. Auf der Ordinate ist der Druck und auf der Abszisse der Brückenstrom in logarithmischem Massstab aufgetragen. Dabei gilt:

Kurve 1 = Wasserstoff
Kurve 2 = Wasserdampf
Kurve 3 = Luft
Kurve 4 = CF_2Cl_2.

Der Abstand der Kurven entspricht dem Verhältnis aus den Wurzeln der Molekulargewichte. Dies trifft jedoch nur bis zu einem Druck von maximal 10^{-1} Torr zu. Im Gebiet

Fig. 7 shows the scale corresponding with this design. The entire measuring range is subdivided into two ranges: 10^{-2} to 1000 Torr and 10^{-3} Torr to 5×10^{-2} Torr. The switching over from one to the other portion of the scale is done by means of a measuring range switch. Fig. 8 shows the overall view of this instrument together with measuring tube, and Fig. 9 shows the inside.

Dependence upon the kind of gas

With gases other than air, the pointer deflection would have to be theoretically proportional to the root of the molecular weight. Such a dependence is also apparent in the range of lower pressures. Fig. 10 shows the calibrating curves for various gases within the lower pressure ranges. The pressure is plotted on the ordinate and the bridge current on the abscissa in a logarithmical scale. In this,

Curve 1 = hydrogen
Curve 2 = water vapour
Curve 3 = air
Curve 4 = CF_2Cl_2.

The distances of the curves correspond with the ratio of the roots of the molecular weights. This, however, applies only up to a maximum pressure of 10^{-1} Torr. For higher pressures, a definite controlling law cannot be given. For

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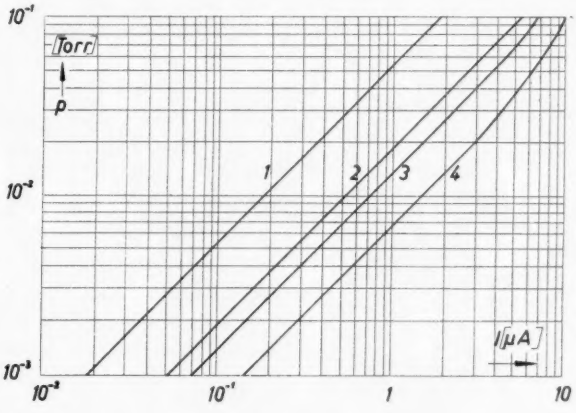

Abb. 10. Anzeige für verschiedene Gase bei niedrigen Drücken.
Kurve 1 = H_2
Kurve 2 = H_2O
Kurve 3 = Luft
Kurve 4 = CF_2Cl_2

Fig. 10. Indication for various gases at low pressures.
Curve 1 = H_2
Curve 2 = H_2O
Curve 3 = air
Curve 4 = CF_2Cl_2

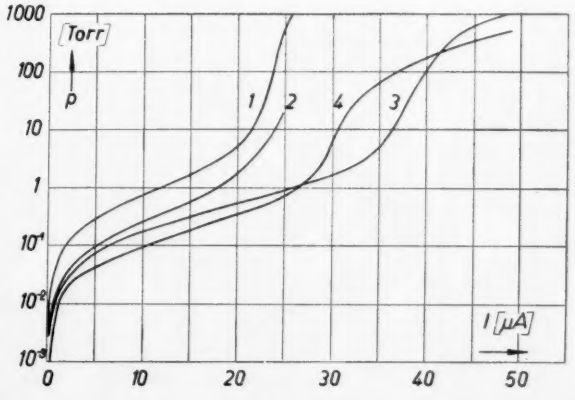

Abb. 11. Anzeige für verschiedene Gase über den ganzen Messbereich.
Kurve 1 = H_2
Kurve 2 = H_2O
Kurve 3 = Luft
Kurve 4 = CF_2Cl_2

Fig. 11. Indication for various gases over the entire measuring range.
Curve 1 = H_2
Curve 2 = H_2O
Curve 3 = air
Curve 4 = CF_2Cl_2

höherer Drücke lässt sich eine eindeutige Gesetzmässigkeit nicht angeben. Für niedridge Drücke kann man also den Eichfaktor für andere Gase als Luft errechnen, während für höhere Drücke eine Eichkurve aufgestellt werden muss. Dies zeigt mit besonderer Deutlichkeit die Abb. 11. Hier wurde der Zeigerausschlag linear und der Druck logarithmisch aufgetragen.

Vergleich mit thermoelektrischen Vakuummetern

Ein Vergleich mit einem thermoelektrischen Vakuummeter zeigt, dass das Reibungsvakuummeter " REVA " einige wertvolle Eigenschaften besitzt. Die Nachteile, die durch die heissen Teile in den Messröhren der thermoelektrischen Vakuummeter auftreten, insbesondere die Zersetzung der Kohlenwasserstoffe, werden bei dem Reibungsvakuummeter " REVA " restlos vermieden, weil sich in der Röhre nur kalte Teile befinden. Die von dem Messband aufgenommene geringe elektrische Leistung bringt eine merkliche Erwärmung nicht hervor. Die Eichung bleibt praktisch konstant. Auch die innere Reibung des Bändchens verändert sich nicht. Wir haben einmal ein Bändchen vorsätzlich verbogen, wodurch die innere Reibung wesentlich vergrössert wurde. Nach mehreren Betriebsstunden hatte sich diese innere Verspannung abgebaut und die Dämpfung langsam ihren ursprünglichen Wert wieder angenommen.

Sämtliche Teile des Messsystems sind vernickelt, um chemische Angriffe weitgehend auszuschalten. Das Messband selbst besteht aus einer korrosionsfesten Platin–Nickel–Legierung. Die Abhängigkeit von der Gasart ist gegenüber einem thermoelektrischen Vakuummeter wesentlich geringer. Beträgt die Abweichung gegenüber Wasserdampf bei einem thermoelektrischen Vakuummeter 1,95, so ist der Faktor bei dem Reibungsvakuummeter " REVA " nur 0,79. Ein thermoelektrisches Vakuummeter zeigt also bei Wasserdampf den 1,95 fachen Wert an, während das " REVA " den 0,79 fachen Wert anzeigt. Einem Fehler von +95% steht ein Fehler von −21% gegenüber.

Die Ansprechzeit bei dem Reibungsvakuummeter " REVA " ist sehr kurz. Der gesamte Einschwingvorgang dauert etwa 3 Sekunden vom Einschalten der Röhre an, während die Zeitkonstante, mit der das Messinstrument einer Druckänderung folgt, etwa 0,2 Sekunden beträgt. Ein weiterer Vorteil ist, dass man das Gerät jederzeit leicht kontrollieren kann. Man braucht nur die Röhre dem Atmosphärendruck auszusetzen und zu kontrollieren, ob das Instrument den herrschenden Atmosphärendruck anzeigt. Sollte das nicht der Fall sein, so kann man annehmen, dass die Fehlanzeige auf den Einfluss grösserer Eisenmassen auf das Magnetfeld zurückzuführen ist. Diesen Einfluss kann man durch einen aussen auf der Röhre angebrachten beweglichen Ring beheben (Abb. 8), indem man ihn in der Längsrichtung der Röhre so lange verschiebt, bis das Gerät den herrschenden Atmosphärendruck anzeigt. Damit ist das Vakuummeter für richtige Anzeige über den ganzen Messbereich justiert.

In der Praxis haben sich die Geräte gut bewährt.

lower pressures, therefore, the calibrating factor can be calculated for gases other than air, while a single calibrating curve must be ascertained for higher pressures. This is clearly shown especially in Fig. 11. Here, the pointer deflection has been plotted linear and the pressure logarithmically.

Comparison with thermoelectric vacuum gauges

A comparison with a thermoelectric vacuum gauge shows that the friction vacuum gauge, " REVA ", features several useful characteristics. The drawbacks resulting from hot parts in the measuring tubes of thermoelectric vacuum gauges, especially the disintegration of the hydrocarbons, are completely eliminated with the " REVA " friction vacuum gauge since the tube is cold throughout. The slight energy absorbed from the measuring ribbon does not cause heating worth mentioning. Calibration remains practically constant, and the internal friction of the ribbon does not change. A ribbon was once bent purposely so that the internal friction was considerably increased. After several hours of operation, however, the internal distortion disappeared and the damping slowly took up its original value.

All parts of the measuring system are nickel-plated in order to resist chemical attacks. The measuring ribbon itself consists of a corrosion-resistant platinum–nickel alloy. Compared to the thermoelectric vacuum gauge, there is considerably less dependence upon the type of gas. If the deflection at the thermoelectric vacuum gauge amounts to 1.95 in the case of water vapour, this factor is only 0.79 with the friction vacuum gauge " REVA ". That is, a thermoelectric vacuum gauge indicates an 1.95-fold value of water vapour while the " REVA " indicates 0.79 of its value. An error of +95 per cent as opposed to an error of −21 per cent.

With the " REVA " friction vacuum gauge, the response period is very short. The time taken for the vibrations to begin is about 3 sec from switching on the tube, while the time constant with which the measuring instrument follows a change in pressure is about 0.2 sec. Another advantage is that the instrument can be easily controlled at any time. It is only necessary to subject the tube to atmospheric pressure and to check whether the instrument indicates the atmospheric pressure. If this should not be the case, then the error is caused by the influence of masses of iron on the magnetic field. This error can be eliminated by means of a ring attached to the outside of the tube (Fig. 8) and by shifting it longitudinally along the tube until the instrument again indicates the atmospheric pressure. The vacuum gauge can thus be adjusted to give correct indication over the entire measuring range.

In practice, these instruments have proved extremely efficient.

Letter to the Editor

Pumping of Hydrocarbons by Ion Pumps

Ion pumps reportedly fail to pump organic vapors. The reasons for this failure have not been clear. Organic vapors gradually evolved in some vacuum systems can in extreme cases cause deterioration of the pump.

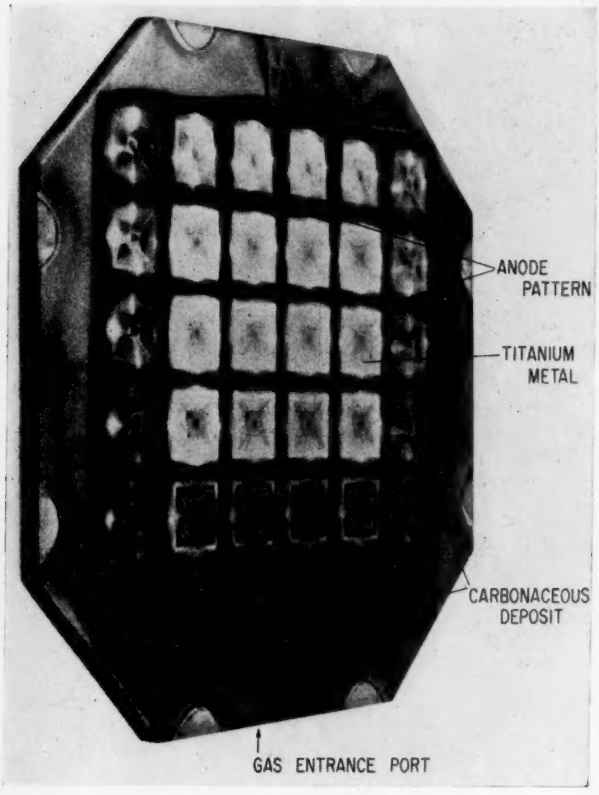

Fig. 1. Cathode of a diode ion pump after pumping benzene at pressures of 10^{-5} Torr.

Experiments in this Laboratory have shown that methane is easily pumped in an ion pump. However, it has been found that if benzene at a pressure of about 1μ is continually admitted to an ion pump, the pressure actually increases and the main gases found by mass spectrometer measurements are chiefly CH_4 and H_2. On examining the inside of the ion pump a carbonaceous deposit, difficult to sputter, is found on the cathodes. Once this layer is formed the normal sorption of gases by sputtered metal ceases and the high voltage Penning discharge simply dissociates the higher molecular weight organic vapor into lower molecular weight species and the pressure increases. The carbonaceous deposit on the cathode builds up faster than it can be removed by sputtering.

At lower pressure (10^{-5} Torr) of benzene or toluene, the ion pump will continue to pump for long times. On examining the cathodes (Fig. 1) it is found that the organic vapor is broken down in the region near the gas entrance port and to some extent around the periphery of the cathodes. The dissociated gases are then pumped in the normal fashion in the cleaner titanium regions of the pump where appreciable sputtering can occur. If the pressure of organic vapor momentarily rises, then the cathodes are covered by the carbonaceous deposit and the pumping action ceases. The discharge then, as before, proceeds to decompose the organic vapor causing the pressure to rise.

Reactivation of the pump is accomplished by admitting oxygen at low pressures and running the discharge. Presumably, the oxygen atoms and ions formed in the discharge react with the carbonaceous deposit on the cathodes forming volatile gases such as CO and H_2O. Since the carbonaceous deposit is difficult to sputter, reactivation by nitrogen or inert gases was not effective in our experiments.

Benzene can be pumped for long times at higher benzene pressures by bleeding air into the pump. The oxygen keeps the carbonaceous deposit from building up on the cathodes and the normal pumping by sputtering can proceed.

J. E. Kelly
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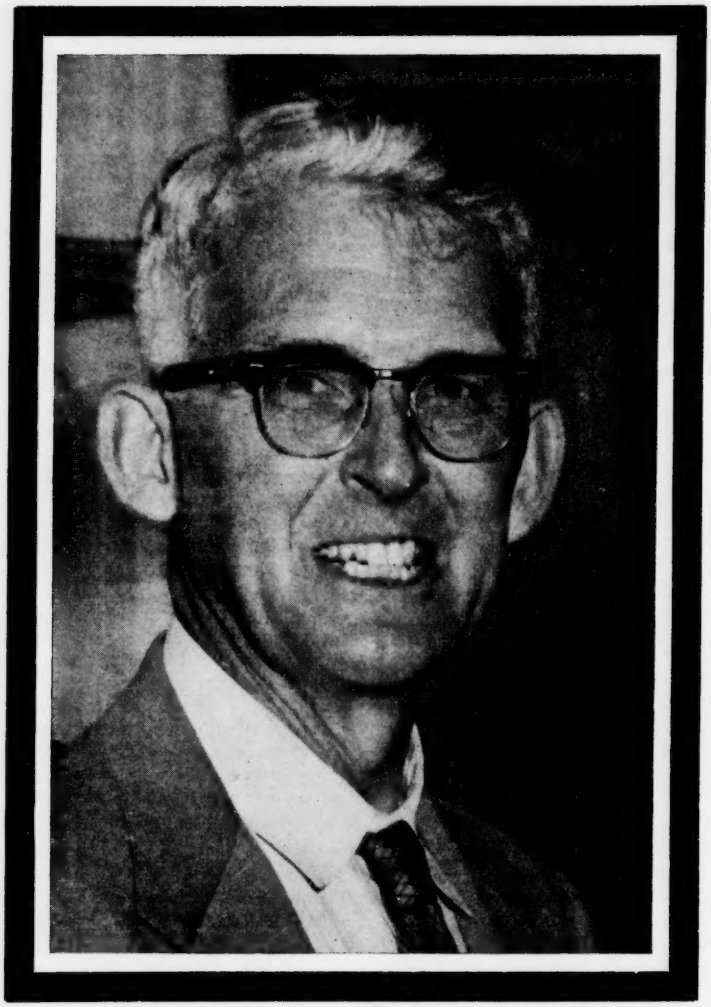
Obituary

C. Robert Meissner
1898 – 1961



As President-Elect of the American Vacuum Society, Robert Meissner had looked forward to taking office as President at the International Congress on Vacuum Science and Technology in Washington, D.C. on 16–19 October. He had been elected to this office in recognition of his contributions to vacuum technology and his outstanding service to the American Vacuum Society as Program Chairman and Editor of the Transactions for the years 1959 and 1960, as well as for his dynamic personality and interest in the work of the A.V.S. News of his death on 16 June, 1961 came as a shock to the writer and to the other members of the Board of Directors of the Society who had counted on his help in organizing the International Congress in Washington and had known him as a friend and co-worker.

At the memorial service held for Robert Meissner in Atlanta, Georgia, Dr. Vernon Crawford, Director of the Georgia Tech. Engineering Experiment Station, delivered a tribute from which we quote the following portion :

" His field of specialization was high vacuum technology and he approached his work with an enthusiasm, an imagination, an ingenuity, and a flair which I have never seen surpassed. In the two brief years he was employed at Georgia Tech. his contributions were substantial and lasting. He designed, and in large part constructed, a high vacuum laboratory. He organized, directed, and participated in a series of seminars in vacuum science which measurably increased the professional stature of the Georgia Tech. Faculty members and students

who participated in it. Just before his death he was in the process of acquiring for the school a vacuum laboratory to be used for educational purposes. I am confident that this work will be carried to completion by others. His professional achievements at the Bell Telephone Laboratories in New Jersey, where he worked for many years before coming to Atlanta, are too numerous to detail here. His standing among those best qualified to judge the quality of his work is revealed by the fact that for the past few years he has been one of the directors of the American Vacuum Society and for the past year has been President-Elect of that organization.

" No one can deny that he was an extremely gifted engineer. But to those of use who knew him well he will always be remembered as a great human being. We will not forget his never-failing good humour, his ready smile, his infectious laugh, and his special twinkle for children. We will remember his willingness to share our problems, and his unwillingness to burden us with his own. We will remember the quiet dignity with which he rose above the vexations, frustrations, and vicissitudes to press on to the goal in spite of obstacles, and remembering, we will perhaps be able to recreate something of his spirit within ourselves."

Mr. Meissner was born in Hamburg, Germany, on 20 November 1898 and received a B.S. degree in Electrical Engineering at the University of Pennsylvania in 1923. As a member of the technical staff of the Bell Telephone Laboratories from 1921 to 1959 his work covered electronics, solid state physics, and vacuum techniques as applied to thin films for electronic circuit components. In 1959 he transferred to the Engineering Experiment Station of the Georgia Institute of Technology where he set up a vacuum laboratory to continue his thin film studies as noted above.

The writer feels a deep sense of personal loss, having come to know Bob as a cheerful friend and energetic co-worker who spent many hours editing manuscripts, checking galley and page proofs, and corresponding with the publisher as Editor of the A.V.S. Transactions. Mr. Meissner was also a member of the Honorary International Editorial Advisory Board of the journal *Vacuum*. He designed a simple but effective refrigerated trap for improving the vacuum in bell jars which is now commonly referred to in the literature as the " Meissner Trap ". He was truly dedicated to the advancement of vacuum science and technology.

BENJAMIN B. DAYTON

President, American Vacuum Society

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Conference

THE Second Czechoslovak Conference on Electronics will be held in Prague, 24–26 April, organized by Charles University, the State Committee for Technical Development and the Union of Czechoslovak Mathematicians and Physicists. The Conference will work in the following sessions : Electron and Ionic Optics, Gaseous Electronics and Plasma Physics, Electron Emission and its Applications, Physics, Techniques and Technology of High Vacuum, Microwave Tubes and Circuits.

Address of the Organization Committee : Prague 2, Ke Karlovu 5.

Abstracts

General Vacuum Science and Engineering

10. Vacuum Science and Technology

10

1. High Vacuum Equipment.
Short report in *Engineer*, **210**, 5463, p. 604, 7 October, 1960.

11. Production of Low Pressures

11

2. Ultimate Pressure in Ultra-high Vacuum Systems. *Netherlands.*
Various factors influence the realization of extremely low pressures in vacuum systems and limit the attainable pressure. Some of these are of a physical or chemical nature, but considerations of simplicity and ease of attainment must be taken into account in special cases. In this paper, the more general aspects will be treated and the importance of various factors in different cases will be discussed. (Author)

A. Venema, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

11 : 21

3. A Hypothesis Concerning Limitations of Diffusion Pumps. *United States.*
An examination is made of the wide discrepancy between theoretical and actual performance of diffusion pumps and of the reasons adduced for this discrepancy. A new hypothesis is offered, according to which the relatively high pressures persisting on the high-vacuum side of diffusion pumps result from the backstreaming of large numbers of molecules carried on compression waves originated by eruptive boiling. This hypothesis accounts for the relative ineffectiveness of baffles and for several other previously unexplained phenomena. Evidence supporting the hypothesis is given, remedial measures are suggested, and implications for many vacuum applications are briefly outlined. (Author)

P. B. Kennedy, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

11 : 47

4. Investigations Concerning Bulk Getters from Metals of the IVth A Group and Thorium. *Italy.*
The gettering properties of metals of the IVth A group and thorium, as well as some of their alloys, are investigated for a number of gases. Particular attention is paid to the dependence of gettering on temperature. The experimental measurements have been carried out at pressures of the same magnitude as encountered in large scale industrial production of electron tubes. The possibility of employing some of the alloys investigated as bulk getters is discussed. The activation conditions and the range of temperatures in which these getters may be satisfactorily employed are considered. Finally particular attention is paid to those conditions which render these getters stable and give the minimum outgassing within the tube during the preliminary operations. (Author)

P. della Porta and S. Origlio, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

11 : 21 : 16 : 20

5. Barium Absorption Pumps. *United States.*
The use of large quantities of evaporated barium in combination with ionization makes a vacuum pumping system of basic simplicity and of high speed for some gases. The relatively low evaporation temperature of barium permits a simple, externally heated metal vacuum flask. Experiments with several different pumps indicate very high pumping speeds for hydrogen and oxygen, but the speed for noble gases and some organic vapors is limited by the ionization rate. In some cases a parallel diffusion pump is used to pump impurities of non-absorbable gases. The pumping speed of several gases has been investigated as a function of gas pressure and thickness of the barium layer. The mechanism of gas absorption is discussed in the light of the experimental results. (Authors)

R. W. Cloud, H. Milde and S. F. Philp, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

11 : 21 : 20 : 32

On an Oil Self-Purifying Diffusion Pump System. See Abstr. No. 65.

11 : 21 : 18

Preliminary Pumping Results with Penning-type Discharges Supported on Condensable Metal Vapors. See Abstr. No. 73.

11 : 21 : 22 : 18

Pressure-versus-Time Variation in Closed Vessels Exhausted by Ionic Pumping. See Abstr. No. 74.

12. Measurement of Low Pressures

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6. A Serious Error Caused by Mercury Vapour Stream in the Measurement with McLeod Gauge in the Cold Trap System. *Japan.*
In the calibration of ionization gauges against the standard McLeod gauge, it has been observed that the sensitivity of the ionization gauge varies with the room temperature in many experiments, sometimes up to 25 per cent. It is found that this phenomenon is due to the mercury vapour stream from the McLeod gauge to the cold trap inserted in the line to the ionization gauge manifold. Theoretical treatment by means of the diffusion of nitrogen in the mercury vapour stream sufficiently agrees with experimental results. A way to remove this obstacle is to cool the cut-off position of the McLeod gauge. Some analogous problems on vacuum technique are discussed. (Authors)

H. Ishii and K. I. Nakayama, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22

7. Accurate Calibration of Vacuum Gauges to 10^{-9} Torr.
Apparatus for the accurate calibration of vacuum gauges at pressures from 10^{-3} to 10^{-9} Torr has been constructed. The system involves a cascade of differentially-pumped stages with carefully defined orifices. Operating in the molecular flow

region, a low pressure at the gauge under test can be referred to a McLeod gauge operating at a higher pressure in a range favorable to it. Pressure ratios up to 10^5 between the McLeod gauge and test gauge have been obtained. (Authors)

J. R. Roehrig and J. C. Simons, Jr., *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22 : 21

8. Pressure Measurement in Non-Baked Ultra-high Vacuum Systems. *United States.*

The use of high speed cryogenic pumping systems has resulted in the obtaining of pressures in the ultra-high vacuum region without the use of a bakeout. Under these conditions two new pressure measurement problems are introduced due to directional pressure effects and outgassing of the gauge tubulation. These effects can cause reading errors in excess of one decade. This paper discusses these effects. A solution is presented which eliminates both types of errors and hence allows for improved pressure measurement in non-baked ultra-high vacuum systems. (Author)

D. J. Santeler, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22 : 18

9. Electrical Cleanup in Ionization Gauges. *United States.*

At equilibrium pressure in an ionization gauge the number of ions penetrating the glass is balanced by the atoms diffusing out of the glass. The number diffusing out is a function of the number of atoms in the glass and their concentration distribution. At equilibrium the rate of recovery is proportional to $n_0 t^{-\frac{1}{2}}$; where n_0 is the total number of atoms cleaned up, and t is the recovery time. A detailed analysis of the temperature dependence and diffusion behavior will be presented. (Authors)

K. B. Blodgett and T. A. Vanderslice, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22

10. Design Parameters' Influence on M.I.T.-Bayard–Alpert Gauge sensitivity. *United States.*

The Bayard–Alpert gauges studied all had a screen grid between the electron emitting filament and the glass wall. Ion currents observed at the normal, small wire ion collector inside of the electron collector and also on the screen were studied as a function of the electron emission current as measured at the filament and the pressure of nitrogen. The parameters investigated were the distance between the electron emitting filament and the electron collector, and the design of the electron collector. Although the ion current observed at the normal collector showed a strong nonlinearity with increasing electron current at higher pressures, the total ion current was remarkably linear. Gauge sensitivity K decreases by a factor of two as the filament-to-electron collector spacing is reduced from 3 mm to 1 mm. The closing of the electron collector with fine wires increases the sensitivity by a factor of 3.1 compared to the open-ended structure. At the high pressure of $p = (10^{-1}$ Torr), the gauge constant decreases and the limit of pressure variation detection comes at $Kp = 1.7$ for a 100 V electron acceleration potential. (Author)

W. B. Nottingham, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22 : 18

11. A Precise Method to Determine Pressures in High Vacuum. *Germany.*

The scattering of a molecular beam in a gas volume effects a decrease of beam intensity. This is a well-defined function of the density of gas along the beam-path. Therefore the scattering can be taken to determine the gas pressure. The scattering cross-section cannot be calculated exactly; therefore this method gives primarily accurate relative determinations. Once compared with an absolute manometer, such beam apparatus can be used for calibrating measurements. Measurements of the relative sensitivities of different ionization gauges with various operating conditions illustrate the applications of this method. (Authors)

R. Helbing, R. Jaeckel and H. Pauly, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22 : 18

12. The X-ray Limit in Ionization Gauges. *Germany.*

For the X-ray limit in ionization gauges the equation $p_{\min} = 10k_x/k_g$ is obtained with k_x the photoelectron constant and k_g the gas ion constant. A theoretical analysis of the quantity k_x is performed taking into account the X-ray emission due to electron bombardment of the electron collector and the release of photoelectrons at the ion collector. k_x is shown to be proportional to the nth power of the electron collector voltage in satisfactory agreement with experimental results. The exponent n depends mainly on the properties of the ion collector material and falls between $n = 1$ and 2. The constant of proportionality is dependent upon the tube geometry and to a lesser degree upon the electron collector material. Experimental investigations were carried out with receiving tubes, ionization gauges and specially assembled test tubes. Methods to reduce the X-ray limit are discussed. (Authors)

H. J. Schütze and H. W. Ehlbeck, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22 : 24

13. Use of a Standard Orifice in the Calibration of Vacuum Gauges. *United States.*

A vacuum gauge calibration facility is described in which known pressures in the 10^{-3}–10^{-6} Torr range can readily be obtained by admitting gas at measured rates into a test chamber which is continuously pumped through an orifice of known area at a speed that can be calculated. Pressures derived in this way are compared with sensitive McLeod gauge measurements showing excellent agreement and certain advantages of the orifice method. Summaries are given of calibrations that have been made of conventional types of ionization gauges, several types of "nude" gauges, and of gauges operating in magnetic fields. (Author)

C. E. Normand, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 22

14. Absolute Measurement of High Vacuum. *Japan.*

The method of precision measurement of gaseous pressures in the range from 10^{-3} to 10^{-7} Torr is discussed. The instruments used are of the deflecting leaf type, of the plane-vane, and of the cylindrical vane type of Knudsen gauges. The sensitivity variation due to changes of accommodation coefficients, and the effects of surface treatment of the heater and the envelope are also reported. The method of extending the measuring range of the Knudsen gauge to ultra-high vacuum region is also discussed. (Author)

M. Onchi, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

12 : 21

15. Response Time of Thermal Conductivity Vacuum Gauges.

The response time of vacuum gauges may be specified in several ways and it appears that some better understanding—or agreement—is needed in specifying this characteristic. Experimental results are presented for a variety of thermal conductivity vacuum gauges in the range of pressures from 10^{-3} to 20 Torr. Two differently defined response times are suggested, both of which are useful in specifying the characteristics of a particular

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vacuum gauge. These two response times may differ widely in value but are representative of working conditions. (Author)

J. M. Benson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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Adsorption of Molecular Gases on Surfaces and its Effect on Pressure Measurement. See Abstr. No. 30.

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An Ultra-high Vacuum Gage Calibration System. See Abstr. No. 48.

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General Observations on Hot Filament Ion Gauge Operation in Homogeneous Magnetic Fields. See Abstr. No. 77.

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A Vacuum Manometer Using Ultraviolet Light. See Abstr. No. 78.

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Further Developments in the Hot-Cathode Magnetron Ionization Gauge. See Abstr. No. 79.

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A Bayard-Alpert Type Ionization Gauge with a Low X-ray Limit. See Abstr. No. 80.

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An Ionization Gauge for the Measurement of Ultra-high Vacua. See Abstr. No. 81.

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Hp and H/Dp Ions in the Omegatron. See Abstr. No. 82.

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A Comparison of the Partial-Pressure Meters Topatron and Omegatron. See Abstr. No. 83.

12 : 22 : 18

The Mass Filter Partial-Pressure Vacuum Gauge. See Abstr. No. 87.

14. Kinetic Theory of Gases

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16. Vacuum Flow of Gases Through Channels with Circular, Annular and Rectangular Cross Sections. *United States.*
Vacuum flow of hydrogen, helium, air, carbon dioxide and freon-12 was measured in copper channels. These channels included a circular section with a 3.64 cm radius, two annular sections formed by inserting cores of 1.905 cm and 3.174 cm radii into the circular section, respectively, and a rectangular section 0.324 cm by 22.86 cm. In each section the flow was found to approach the molecular-flow limit with decreasing pressure, but the degree of approach depended on the shape of the section. For rectangular channels the agreement with the predictions of Barrett and Bosanquet became poorer as the channel was made more narrow. The data approached the slip-flow limit with increasing pressure in all the channels. The experimental data were fitted over the entire range with empirical equations of the form

$$Q = Q_L + KQ_A\left[\frac{1 + C_1(X/\lambda)C^2}{1 + C_1(16K/3\pi)\,(X/\lambda)C_2}\right]\left[\frac{2}{f} - 1\right]$$

where Q_L is the laminar flow term, KQ_A is the predicted molecular flow rate for diffusely reflected molecules, X/λ the Knudsen number, and f is the fraction of the molecules diffusely reflected. The data from the rectangular section were fitted with $C_1 = 1.23$ and $C_2 = 0.3$. A general empirical equation for annular and circular sections was obtained with $C_1 = 0.275 + 1.27\,b/a$ and $C_2 = 0.4$. The fraction of molecules diffusely reflected from copper surfaces was found to decrease slightly with increasing molecular weight. By assuming $f = 1$ for hydrogen, values of f were calculated to be 0.99 for helium, 0.97 for air and carbon dioxide, and 0.90 for freon-12. Equations for slip flow in annular and rectangular sections were derived and compared with experimental data. (Authors)

W. Dong and L. A. Bromley, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

14 : 51

17. Molecular Flow at Very Low Pressures. *Germany.*
The applicability of the Knudsen law in the ultra-high vacuum range is proved by means of investigations on the capillary flow of helium. Deviations from the Knudsen law, especially a temperature-dependent "seepage" of particles into the wall could not be detected. From the initial flow at low temperatures, some specifications concerning adsorption time of helium atoms at the wall can be derived. The flow of water vapor is of a different nature. The full amount of the Knudsen flow could not be attained owing to a strong temperature-dependent adsorption of the particles on the wall. (Authors)

H. L. Eschbach, R. Jaeckel and D. Müller, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

14 : 15 : 24

18. Improving the Accuracy of Metering Gas Flow and Computing Throughput. *United States.*
Metering gas flow in vacuum applications, while generally accepted as a simple measurement, is one which can easily be a source of sizeable error. Conventional oil burette apparatus under certain conditions of use, can be in error as much as 20 per cent. Techniques of proper usage and methods of correction are discussed. An improved gas flow metering device is described that can reduce the variations to less than 0.5 per cent over an extremely wide range of flow rates. Other small errors that can affect gas flow meter measurements and enter into throughput computations are also discussed. (Author)

D. L. Stevenson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

14 : 16

19. Automatic Apparatus for Measuring Gas Evolution Rates. *United States.*
A technique and automatic apparatus for measuring gas flow rates at pressures around 1–5 microns Hg is described. The apparatus is particularly suited to studies of the permeability and diffusivity of gases in metals. The results obtained are more precise and reliable than those obtained by manual operation of such equipment. (Author)

M. L. Hill, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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The Measurement of Accommodation Coefficients of Gases on Tungsten. See Abstr. No. 33.

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Standard Leaks and Their Calibration by Constant Pressure Change in Volume Techniques. See Abstr. No. 108.

15. Fluid Dynamics

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Vacuum Flow of Gases Through Channels with Circular, Annular and Rectangular Cross Sections. See Abstr. No. 16.

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Improving the Accuracy of Metering Gas Flow and Computing Throughput. See Abstr. No. 18.

16. Gases and Solids

16 : 52

20. Adsorption of Gases on Germanium.
The adsorption of hydrogen, carbon monoxide, nitrogen and carbon dioxide on germanium films has been investigated. With hydrogen, there is a small activated adsorption on atomizing the gas, extensive chemisorption occurs at a rate controlled by surface diffusion of the adatoms. The rate of desorption, however, is determined by the energy to free the complex from the surface. Carbon monoxide and nitrogen are reversibly, physically adsorbed with an isosteric heat of 3 kcal. With carbon dioxide, carboxylate ion formation predominantly occurs at lower temperatures ; at higher temperatures, carbon monoxide is evolved leaving chemisorbed oxygen. The kinetics and the thermodynamics of these two processes are discussed. (Authors)

M. J. Bennett and F. C. Tompkins, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16 : 47

21. Outgassing Rate of Contaminated Metal Surfaces. *United States.*
Successive evaporation of various molecules from a heterogeneous layer of surface contamination can result in an outgassing rate which is inversely proportional to the time of pumping. A relatively uniform distribution of the activation energies of desorption will result in a sum of the individual outgassing curves for constant desorption energy which appears as a straight line with a slope of minus one on the log-log plot of outgassing rate vs. time of pumping. This line forms an " outgassing barrier " which limits the ultimate pressure in unbaked metal vacuum systems. (Author)

B. B. Dayton, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

22. Desorption of NS22S Stainless Steel by Flash Filament Technique in Ultra-high Vacuum. *France.*
Sorption phenomena on NSS2S stainless steel have been investigated by the so-called flash-filament technique. Desorption of CO, H_2, N_2 were concerned and partial pressures were measured with an omegatron tube. The principle of the method the experimental arrangement and the preparation made of the samples are described. Numerous desorption recordings have been made for different previous histories of each sample. With the help of some hypothesis, a discussion of the results leads either to an order of magnitude of the energy level of surface adsorption, or to a distribution of the gas density in the bulk of the sample. The experimental work is still in progress. (Authors)

D. A. Degras, A. Schram, B. Lux and L. A. Petermann, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

23. The Clean Surface Approach to Adsorption Studies. *United States.*
In view of the intimate relationship between adsorption properties and the surface condition of a solid, considerable research has been devoted to the preparation of single crystal surfaces which are initially atomically clean. Several high-vacuum techniques which have been used for this purpose and several methods which have been employed to evaluate the degree of surface cleanliness and perfection are discussed and compared. Examples of the types of information provided by such experiments are drawn from the extensive measurements which have been made of the properties of semiconductor crystal surfaces. (Author)

J. A. Dillon, Jr., *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

24. Molecular Processes in Adsorption on Metals. *United States.*
The macroscopic kinetics and energetics of the elementary atomic processes occurring on metal surfaces are examined experimentally. More complicated events, such as adsorption and evaporation of molecules, as well as molecular dissociation and reconstitution, are then analysed using the empirical information available on atomic events. The dependence of molecular interactions upon the detailed atomic structure of metal surfaces, as well as the presence of multiple binding states, are finally presented, as revealed by flash desorption and field ion microscopy. (Author)

G. Ehrlich, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

25. Gas Desorption at Rubbing the Surfaces in High Vacua. *Poland.*
In the course of experimentation with very high vacua the desorption of some quantities of gas was observed when glass or metal surfaces were mutually rubbed. A simple experiment consisted, for instance, in placing a small cylindrical metal or glass rod inside a Bayard–Alpert type ionization gauge which after baking and outgassing was cut off from the pump. When the bulb is stirred, the rod moves across the bulb walls, liberating the superficial gas, and the pressure increases. After a time the gas can be re-adsorbed with gauge voltages switched off and the pressure decreases. (Author)

J. Groszkowski, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

26. The Interaction of Rare Gas Atoms with Surfaces. *United States.*
At relatively high temperatures the interaction between the adsorbent and adsorbate molecules is simple enough to permit a virial expansion of the apparent p–V product. If simple rare gas molecules are used, theoretical calculations of some of the virial coefficients can be made for relatively sophisticated potential functions. An extremely accurate gas thermometer was used to investigate low area powder of a defined nature. Some of the information that comes from measurements of this kind are the heat of adsorption of a single atom on a surface, a test of the theories of van der Waals forces, the distance of closest approach of atoms to surfaces, and a new way of estimating the area of a well-characterized surface. (Author)

G. D. Halsey, Jr., *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

27. Physical Adsorption in Ultra-High-Vacuum Systems. *Canada.*
Extremely low pressures ($p \leqslant 10^{-20}$ Torr) can be achieved by cooling ultra-high-vacuum systems to liquid helium temperatures. The ultimate physical mechanism involved is physical adsorption of the residual gases on the cold surfaces. A discussion will be given, based on the author's own work, of the laws of physical adsorption as they apply to ultra-high-vacuum systems, and of various ways in which these laws may be applied in such systems. (Author)

J. P. Hobson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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16 : 47

28. The Desorption of Ionically Trapped Argon from Tungsten.
A thoroughly clean tungsten wire target was bombarded with singly charged mono-energetic argon ions in the energy range 80–4000 eV. The argon atoms trapped in the tungsten were thermally desorbed into a known volume containing no significant argon pumps. Two modes of heating were used : (a) rapid flashing to 2400°K, and (b) uniform, slow heating rate (50°K/sec) to 2400°K. The former experiments yielded values of ion sticking probability and entrapment saturation numbers ; the latter gave activation energies of desorption. Four desorption peaks were observed whose amplitudes depended on the bombarding ion energy, but whose temperatures did not.
(Author)

E. V. Kornelsen, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

29. Adsorption on Semiconductors. *United States*
The problems involved in studying adsorption on semiconductors are quite different from those normally encountered with metals. The effect of minute amounts of impurities in the solid near the solid–gas interface is greatly enhanced when the carrier concentration is low (i.e. 10^{14} carriers cm^{-3}). This means that one must strive for chemical uniformity right up to the interface and at the same time produce a clean surface. The effects of charge transfer between an adsorbing particle and the semiconductor will be discussed. Here again, the observed effects are due to the low charge density in the semiconductor. This latter fact, however, opens up a whole set of measurement techniques such as field effect, photoconductivity and surface conductivity. The experimental and theoretical treatment of these measurements will be described for substrates of silicon and germanium. (Author)

J. T. Law, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16 : 12

30. Adsorption of Molecular Gases on Surfaces and its Effect on Pressure Measurement.
Measurements of the rate of adsorption of various molecular gases on clean metallic surfaces have been related to measured values for the pumping speeds of a well-outgassed ionization gauge. Estimates have been made of the nature and magnitude of errors in pressure measurement attributable to adsorption on the surfaces of ionization manometers. For some gases, such as nitrogen, the necessary correction is negligible ; for others, such as carbon monoxide, the correction may be large and unpredictable. Experiments to detect surface ionization in a normally-outgassed Bayard–Alpert gauge have failed to yield a detectable effect, even when the electrodes have been subsequently saturated with carbon monoxide. In general ultra-high vacuum use, ionization manometers, whether for total or partial pressures, properly measure the volume density within the gauge. However, if the conductance to the system volume is small, the pressure within the gauge may not be identical to that in the system. Reasonable corrections can be made if the reactions between gases and gauge surfaces are understood.
(Authors)

D. Lee, H. Tomaschke and D. Alpert, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

31. Modern Vacuum Technology and Surface Interactions. *Italy.*
The importance of the study of surface interactions for a further development of vacuum technology is emphasized, as well as the need for better application to vacuum technology of the experience accumulated by the research work in physical chemistry. Outstanding problems in the field of gas–metal interactions are briefly reviewed and recent findings, both in experimental and theoretical works are summarized. (Authors)

A. G. Nasini and F. Ricca, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

32. Gas Permeation Through the Vacuum Envelope. *United States.*
The relationships and available values for permeation rate, diffusion constant and solubility of various gases and solids are discussed. Values are given for walls of glass and metal in differing external environments. Some generalizations can be formulated. True permeation through the wall is due to solution and then diffusion in the wall material. Experiments to measure it must be carefully devised to distinguish its effects clearly from various other gas sources as real leaks, pump back-streaming, gas originally in and on the wall material, electrolysis in glass walls or oxide dissociation effects. Criteria are given for making sure true permeation is being measured. (Author)

F. J. Norton, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16 : 14 : 40

33. The Measurement of Accommodation Coefficients of Gases on Tungsten. *United Kingdom.*
The temperature of the tungsten wire maintained in an ultra-high vacuum is raised by the passage of direct current. An alternating current of negligible heating effect is superimposed on this direct current. The resistance of the wire on exposure to the inlet gas is measured with an a.c. bridge employing a differential amplifier and a cathode ray oscillograph display relatable to change of wire temperature with time. Results are given for the noble gases on clean tungsten and on tungsten which has previously sorbed a monolayer of another gas.
(Authors)

A. E. Saunders and J. Yarwood, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16

34. Adsorption and High Vacua. *United Kingdom.*
The paper outlines the more important features of chemisorption and physical adsorption. In chemisorption studies preparation and maintenance of a clean surface is vital. Recent measurements of velocities and heats of chemisorption are described and their significance discussed. Mechanisms of chemisorption and the mobility of chemisorbed layers are mentioned, together with heterogeneity of metal surfaces. The need for further work on carbon using modern techniques is mentioned. The simpler nature of physical adsorption is emphasized, and recent work on isotherms and on surface mobility mentioned.
(Author)

B. M. W. Trapnell, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16 : 21

35. Some Low Pressure Sorption Characteristics of Evaporated Titanium and Zirconium with Dry Air and Oxygen. *United States.*
The room temperature sorption of dry air and oxygen by evaporated titanium and zirconium films was measured by the dynamic capillary flow technique. Films were formed at dynamic ambient pressures of 10^{-8} Torr or less. Speeds of ion gauge pumping were determined and used to obtain true gettering rates. The initial gettering rates, changes in rates with amount sorbed, and sticking coefficients were measured in the pressure range 10^{-4}–10^{-8} Torr. Films studied ranged in thickness from about 10 to 1 μg/cm. (Authors)

E. J. Zdanuk and S. P. Wolsky, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16 : 31

36. Degradation of Glass Vacuum Tubes Resulting from Storage in a Helium Atmosphere. *United States.*
The inert and high diffusive characteristics of helium gas has proved deleterious to vacuum tubes used in electronic circuitry which have been sealed in a helium rich environment. A generalized expression is derived from Fick's law relating the internal pressure rise vs. time for the helium permeation through the glass wall of the tube. Using a standard commercial glass vacuum tube as an ionization gauge, the pressure rise as a result of a "soak" in prue helium at several atmospheres is monitored. The effect on hard vacuum tubes and thyratrons is discussed with the particular remedy used. (Author)

J. J. Rode, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

16 : 18

Desorption of Gas by Photons. See Abstr. No. 38.

16 : 21

Desorption of Adsorbed Gas and Re-emission of Gas Previously Pumped by Ionic Pumping. See Abstr. No. 54.

16 : 21

Performance Criteria for Sorption Pumps. See Abstr. No. 57.

16 : 25

Mechanism and Properties of a New Device to Reduce Backstreaming of Hydrocarbon Molecules. See Abstr. No. 101.

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Adsorption Capacities of Some Room-temperature Trap Materials. See Abstr. No. 102.

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The Origins and Composition of the Limiting Gas Load in Ultra-high Vacuum Systems. See Abstr. No. 209.

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Outgassing. See Abstr. No. 211.

16 : 11 : 21 : 20

Barium Absorption Pumps. See Abstr. No. 5.

16 : 14

Automatic Apparatus for Measuring Gas Evolution Rates. See Abstr. No. 19.

16 : 21 : 20

A Large-scale Getter Pumping Experiment Using Vapor Deposited Titanium Films. See Abstr. No. 75.

16 : 37 : 30

The Application of Liquid Metal Circulating Systems in Vacuum Technology. See Abstr. No. 195.

17. Thermodynamics

17 : 42

37. High Temperature Reactions of Silica-Glass with Several Metals in a Vacuum. *Japan.*
This paper deals with the high temperature reactions of silica-glass with several metals in vacuum. It was observed through a microscope that the contact angle varies with temperature and that metals penetrate into silica-glass. Aluminum starts the penetration near ~800°C, and spreads rapidly on the surface of silica-glass near 1100°C. This phenomena of penetration was observed in the case of alloying of aluminum with copper, tin, titanium, etc. As a material for successful sealing of metal to silica-glass, indium–silver–titanium alloy is satisfactory. Minimum titanium content in alloys is ca. 0.1 per cent in the experiment. (Author)

H. Okamoto, *Tronsactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

17 : 21 : 34

Application of Liquid Helium Cryopumping to Large Electric Rocket Vacuum Facilities. See Abstr. No. 51.

17 : 21

The Formation of Hydrocarbon Gas by Titanium Getters Containing Carbon and Hydrogen Impurities. See Abstr. No. 55.

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Experimental Evaluation of High-Vacuum Condensers in Large Vacuum Facilities. See Abstr. No. 56.

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Space Thermal Environment Simulation Facilities. See Abstr. No. 179.

17 : 34 : 20 : 21

Design and Operating Criteria for Environmental Vacuum Chambers. See Abstr. No. 180.

17 : 21 : 52

A Catalytic Method for Cryopumping Hydrogen. See Abstr. No. 72.

18. Gaseous Electronics

18 : 16

38. Desorption of Gas by Photons. *United States.*
The release of adsorbed gas by photon bombardment has been studied for the system CO on Ni. It is found that the probability is of the order of 10^{-8} gas particles released per incident photon for photon energies of a few eV. The effect of outgassing due to bulk heating is shown to be distinguishable from, and negligible in comparison to, the photodesorption process under the experimental conditions. (Authors)

W. J. Lange and H. Riemersma, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

18 : 33

39. Positive Ion Bombardment of Metal Surfaces. *United Kingdom.*
Experimental results are reported on the sorption of neon, argon and krypton ions by molybdenum, platinum and tungsten surfaces. The measurements have been made on ribbon targets using monochromatic ion beams with energies up to 3 keV. Observations have also been made upon the replacement of a sorbed gas by bombardment with ions of a different gas. A simple analysis has shown the results to be consistent with the mechanisms of sputtering and ion penetration and has enabled a quantitative estimate of the depth distribution of the incident ions to be made in terms of the sputtering coefficients of the metals. (Authors)

J. S. Colligon and J. H. Leck, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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18 : 33

40. Electrical Cleanup by Excitation of Metastable States. *Germany.*

There exists a great deal of uncertainty as to what portion of the pumping speed, measured in hot cathode discharge tubes, is being contributed by excitation of metastable states in the gas. To answer this question the pumping speed for nitrogen was determined with a special gauge with acceleration voltages between 0 and 35 V. The pumping speed was measured by a difference method which is very sensitive and which is not affected by desorption, small leaks, etc. To achieve this it was necessary to pick up small pressure changes with the ionization gauge. The results give strong evidence that cleanup below 35 V is mainly due to the excitation of the metastable states of molecular nitrogen. (Authors)

R. Jaeckel and E. Teloy, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

18 : 21 : 22

Electrical Cleanup in Ionization Gauges. See Abstr. No. 9.

18 : 12 : 22

A Precise Method to Determine Pressures in High Vacuum. See Abstr. No. 11.

18 : 12 : 22

The X-ray Limit in Ionization Gauges. See Abstr. No. 12.

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A Large Differential Pumping System. See Abstr. No. 46.

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Dynamic Pressure Stages for High-pressure/High-vacuum Systems. See Abstr. No. 47.

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One Year of Operating Experience with Seventy Getter-Ion Pumps. See Abstr. No. 67.

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Some Experimental Data on Parameter Variations with the Triode Ion Pump. See Abstr. No. 68.

18 : 21 : 11

Preliminary Pumping Results with Penning-type Discharges Supported on Condensable Metal Vapors. See Abstr. No. 73.

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Pressure-versus-time Variation in Closed Vessels Exhausted by Ionic Pumping. See Abstr. No. 74.

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The "Secondary" Electrical Gas Cleanup Mechanism. See Abstr. No. 84.

18 : 22 : 12

The Mass Filter Partial-pressure Vacuum Gauge. See Abstr. No. 87.

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A New Deposition Technique for Refractory Metal Films. See Abstr. No. 122.

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Sputtering Yields at Medium and Low Energies. See Abstr. No. 130.

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A Theoretical Model of the Sputtering Process. See Abstr. No. 131.

18 : 30 : 33

Ion Beam Apparatus for the Study of Angular Distribution of Sputtered Material. See Abstr. No. 132.

18 : 30

The Sputtering of Copper by N/p as a Function of Pressure and Temperature. See Abstr. No. 133.

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Physical Sputtering. See Abstr. No. 135.

18 : 30

High Energy Sputtering. See Abstr. No. 136.

18 : 32

Problems Associated with Low Pressure Ion Acceleration. See Abstr. No. 160.

19. Radiation

19 : 51

41. Ultra-high Vacuum Ultraviolet Monochromator. *United States.*

A 1 m, normal incidence vacuum ultraviolet monochromator having a sample chamber pressure of approximately 10^{-9} Torr is described. The entrance and exit slits are fixed in space and on Rowland circle. Wavelength is scanned by moving the grating along the circle. This arrangement requires the center of the Rowland circle to move. All moving parts are external to the vacuum chamber. The high vacuum conditions are obtained by several stages of differential pumping from the lamp housing to the sample chamber. The entire monochromator is of stainless steel with welded joints. Interesting vacuum features are the flange design, liquid nitrogen traps and rotary seal. (Authors)

L. Marton, J. A. Simpson, J. A. Suddeth and L. B. Leder, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

19 : 33 : 51 : 52

42. Recent Progress in Vacuum Spectroscopy.

The growing importance of vacuum spectroscopy for the study of molecular structure, physical chemistry, astrophysics, aeronomy and space science has brought, during the last 10 years, a considerable increase in the number of laboratories where spectra in the vacuum ultraviolet are obtained and investigated. During this period the technics of vacuum spectroscopy have been greatly improved and new types of spectrographs, light sources, radiation detectors and accessories have been developed. In the present report recent technological progress and the most important results obtained by vacuum spectroscopy in the above mentioned fields of research have been briefly summarized. (Author)

B. Rosen, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

19 : 30

Tracer Studies of Vapor-deposited ZnS : Ag Phosphor Films. See Abstr. No. 123.

19 : 30

Instrument for the Controlled Deposition of Optical Film Systems. See Abstr. No. 126.

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Thickness Determination of Thick Films with Multiple-beam Interferometry. See Abstr. No. 127.

Vacuum Apparatus and Auxiliaries

20. Pumping Systems

20 : 32 : 27

43. Problems Peculiar to Very Large Systems. *United States.*
Very large vacuum systems may be defined as systems requiring special enclosures for their erection and operation, cranes to lift and handle components, and a multiplicity of various pumps for evacuation. The reported problems confronted in building such systems are : (1) materials and the structural integrity of the vacuum wall, (2) dimensional stability arouud ports and penetrations, (3) designing for differential expansion due to temperature, (4) compatibility of paralleled various pumping units —kinetic, cryogenic, sorption, (5) reliability of components, leak detection and gauging, and (6) abstersion. The Princeton University Stage II Model C-Stellarator vacuum system is taken as a working example of these problem solutions. (Authors)

J. T. Mark and W. G. Henderson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

20

44. Performance of a Double-walled Ultra-high Vacuum Chamber.
An experimental ultra-high vacuum system employing an inner and an outer chamber is described. Its 16 ft³ working volume is somewhat larger than previously reported systems employing this approach. No gaskets are used on flanges on the radiantly heated inner chamber. Pressures of $2\text{–}3 \times 10^{-10}$ and lower have been observed on both exposed and tubulated B-A type ion gauges. Studies of pressure vs. temperature relationships, outgassing rates, leakage rates, etc., are presented. Measurements made to date indicate the steps required to extend the system's capabilities beyond the 10^{-10} Torr range. (Authors)

R. A. Metcalfe and F. W. Trabert, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

20 : 21 : 22 : 33 : 40

45. A Portable High Speed Ultra-high Vacuum System.
A portable all-metal, ultra-high vacuum system has been designed and constructed which achieves 1×10^{-10} Torr at a pumping speed of 800 l/sec, and is free of hydrocarbon contamination. A sorption pump provides the forevacuum for a 25 l/sec ion-getter pump which evacuates the system to below 10^{-8} Torr. The ultimate pressure of 1×10^{-10} Torr is obtained by a liquid helium pump whose air speed is 800 l/sec. An omegatron (resolving power ~45) analyses the residual gases and detects partial pressures between 10^{-11} and 10^{-10} Torr. Besides the major constituent, hydrogen, traces are found of helium, neon, carbon monoxide and methane. (Author)

R. E. Honig, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

20 : 18 : 21 : 28 : 33

46. A Large Differential Pumping System. *United States.*
A high capacity differential pumping system has been designed and constructed for use in connexion with a special electron gun. It is required that this electron beam go from a region at 1×10^{-8} Torr through a 10 cm² aperture into a region at a pressure of 10 Torr. A four-stage differential pumping system is used to bridge this pressure difference and to handle the required gas flow. This system employs a novel rotating shutter arrangement to reduce the throughput and utilizes special ducts to increase the impedance between stages. Design and operation of the system are discussed. (Author)

P. Shapiro, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

20 : 18 : 33

47. Dynamic Pressure Stages for High-pressure/High-vacuum Systems. *Canada.*
It is not always possible to pass intense particle beams from a high vacuum region into the atmosphere or high pressure gas through foil windows. Passages with open holes, approx. 1 mm in diameter, and one or two intermediate pumping chambers have been developed. Considerations suitable for differential pumping systems at low pressures do not suffice. The dynamics of the gas flow must be considered. Enthalpy controlled flow and its shape, rather than friction controlled laminar or turbulent flow, becomes important, with unexpected advantages. Engineering diagrams have been developed and a number of systems built. (Author)

B. W. Schumacher, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

20 : 12 : 22 : 25

48. An Ultra-high Vacuum Gage Calibration System. *United States.*
An ultra-high vacuum system has been developed for the comparison of vacuum gages. Two McLeod gages mounted in separate modules and in a separate furnace provide absolute calibrations down to 10^{-7} Torr and comparisons below this value are achieved by linear extrapolations down to 10^{-9} Torr. Both liquid nitrogen and zeolite traps are proviced and the mercury is purified by distillation into the McLeod gages. (Authors)

G. W. Monk and W. W. Stickney, III, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

20 : 32

49. Ring Magnet Vacuum Chamber System of the Argonne National Laboratory Zero Gradient Synchrotron. *United States.*
This paper will review the development and fabrication programs of the Zero Gradient Synchrotron Vacuum Chamber System. It covers the period from which the basic parameters of the Synchrotron Vacuum Chamber were laid down through the actual fabrication which is now in process. The Inner Vacuum Chamber is unique in its use of a light-weight aircraft material called "Spacemetal". The problems in minimizing eddy currents caused by the rapidly changing magnetic field, vacuum sealing and construction of 54 ft long chambers are discussed. The Oyter Vacuum Chamber is formed by sealing the Synchrotron Magnet Blocks so that a rough vacuum of less than 1 mm can be maintained. (Author)

W. B. Hanson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

20 : 32 : 21 : 24

50. Ultra-high Vacuum System for a Large Electromagnetic Isotope Separator.
A large, all metal vacuum system capable of being baked at 450°C has been built for high purity separation of short-lived isotopes. The 22 ft long system is pumped with oil diffusion pumps through high conductance low loss liquid nitrogen traps. Gold-wire seals are used for all demountable joints. Large aperture straight through bakeable vacuum valves are used for isolating the ion source and collector. Thus, pressures less than 10^{-6} Torr are achieved in 5 min after introducing a sample. Design and operational data will be presented. (Authors)

R. J. Connor, R. S. Buritz and T. Von Zweck, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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Experimental Evaluation of High-Vacuum Condensers in Large Vacuum Facilities. See Abstr. No. 56.

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A High-Vacuum Orbital Simulator. See Abstr. No. 178.

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Space Thermal Environment Simulation Facilities. See Abstr. No. 179.

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Design and Operating Criteria for Environmental Vacuum Chambers. See Abstr. No. 180.

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Barium Absorption Pumps. See Abstr. No. 5.

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Experience with the Vacuum Equipment for the CERN 25 GeV Proton-Synchrotron. See Abstr. No. 61.

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Ring Magnet Vacuum Pumping System for the Argonne National Laboratory Zero Gradient Synchrotron. See Abstr. No. 62.

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Aspects of the Technology of Mercury Vapour Pumping Systems. See Abstr. No. 63.

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On an Oil Self-purifying Diffusion Pump System. See Abstr. No. 65.

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Ultra-high Vacuum Pump Sets. See Abstr. No. 66.

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One Year of Operating Experience with Seventy Getter-Ion Pumps. See Abstr. No. 67.

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A Large-scale Getter Pumping Experiment Using Vapor Deposited Titanium Films. See Abstr. No. 75.

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A Low Pressure Evaporation Plant for Rapid Operation. See Abstr. No. 147.

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An Ultra-high Vacuum System for Low Energy Electron Diffraction Studies. See Abstr. No. 170.

20 : 37

Vacuum Crystal Pulling Installations and Combox Systems for Manufacture of Transistors and Microelectronic Components. See Abstr. No. 197.

21. Pumps and Pump Fluids

21 : 17 : 34

51. Application of Liquid Helium Cryopumping to Large Electric Rocket Vacuum Facilities. *United States.*

An experimental evaluation of a toroid-shaped, 6.46 ft², liquid-helium-cooled cryogenic condensing surface and its application to ion rocket testing in a 314 ft³ ultrahigh vacuum facility is discussed. Data are presented which compare ultimate pressures obtained with a liquid-helium-cooled cryopump with that pressure obtained with a liquid-nitrogen-cooled cryopump operated under varied test conditions. The pumping speeds of these cryopumps are compared with theory. The methods of handling and transporting liquid helium are discussed. The residual gases in the facility are examined with the aid of an omegatron-type mass spectrometer before and during the operation of the cryopumps. (Authors)

R. J. Cybulski, E. A. Richley and T. A. Keller, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 34

52. Evacuating Large Space Chambers with Positive Displacement Blowers. *United States.*

This paper discusses the application of rotary positive boosters to the evacuation of large chambers for the environmental testing of space vehicles. It shows how these boosters are used for rough pumping to a pressure at which fine pumps are able to take over. Parameters (experimentally determined) for stage temperature rise and maximum compression ratio are used to analyse various multi-stage arrangements. A system with a maximum pumping speed of 70,000 ft³/min, as applied to a 100 ft dia. sphere, is described. A formula for calculating pumpdown time during outgassing is given. (Authors)

D. L. Dowling, D. B. Herrick and W. E. Rose, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 25 : 40

53. Low Temperature Cooling Experiments with Ultra-high Vacuum Pumping Units.

Low temperature cooling experiments are made with liquid nitrogen in ultra-high vacuum pumping units which are equipped with diffusion pumps and adsorption traps or creep baffles respectively. When thawing out, a number of pressure increases show up in the course of increased heating which are due to the evaporation of different condensed fractions. After measuring the appearance temperatures and pressures the peaks can be identified by comparison with the vapour pressure diagrams. This method of peak analysis is used in connexion with the problem of saturating adsorption traps. In addition, a mass spectrometer is used to analyse the peaks. (Authors)

J. Hengevoss and W. K. Huber, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 16

54. Desorption of Adsorbed Gas and Re-emission of Gas Previously Pumped by Ionic Pumping. *Canada.*

The rate of desorption of adsorbed gas is examined as a function of the activated energy of desorption and the temperature in a simple model. The model is examined for its qualitative approximation to reality and for practical values of the parameters. Recent results on the re-emission of gas previously pumped by ionic pumping are reviewed, and an assessment is presented of the degree to which this source of gas can be reduced.

(Author)

J. P. Hobson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 17

55. The Formation of Hydrocarbon Gas by Titanium Getters Containing Carbon and Hydrogen Impurities. *United Kingdom.*

The carbon and hydrogen impurities in titanium getters are known to produce hydrocarbons and their formation and nature have been studied using an Omegatron. The gas production by (1) continuous evaporation from a molten titanium droplet heated by electron bombardment in a getter ion pump (2) titanium evaporated from tungsten heaters in an ultra-high vacuum plant, has been studied. During continuous evaporation from a molten titanium droplet intermittently replenished, the

carbon concentration in the molten droplet increased with evaporation time. The principal hydrocarbon gas formed in the system had a mass number of 15 (CH_3). The CH_3 concentration in the system increased each time the molten droplet was replenished with fresh titanium. The gas concentrations measured by the Omegatron were expressed in terms of ion current/electron current (I_i/I_e). Pre-heating and evaporating titanium from tungsten filaments in a hydrogen atmosphere (10^{-7}–10^{-6} Torr N_2 equivalent) produced mainly methane (mass number 16). Two types of titanium with different hydrogen and carbon contents were evaporated from tungsten filaments. The methane production was plotted as a function of atomic and diatomic hydrogen for the three phases, pre-evaporation heating, evaporation and post-evaporation. It was shown that the law of mass action was applicable to methane formation for the first two phases. A plot of the methane concentration $(I_i/I_e)_{CH_4}$ as a function of the total hydrogen concentration $[(I_i/I_e)^2H(I_i/I_e)_{H_2}]$ gave a linear relation for all three phases. In the first two phases two curves were obtained, the slopes of which were dependent upon the carbon content of the getter material. (Authors)

L. Holland, L. Laurenson and P. G. W. Allen, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 17 : 34 : 20

56. Experimental Evaluation of High-Vacuum Condensers in Large Vacuum Facilities. *United States.*

An experimental evaluation of a liquid-nitrogen-cooled, high-vacuum condenser is presented and discussed. Sodium vapor was injected into a stainless-steel, radial-fin condenser at thermal velocities and flow rates of 39–177 g/hr. The condenser had a surface area of 19.2 m^2 and was located in a 1.07 m dia. by 2.13 m electric rocket test chamber, evacuated by a 32 in. oil diffusion pump. Pressures ranging from 5×10^{-8} to 1×10^{-5} Torr are compared with a previous theoretical analysis and other experimental data. Pressure–time dependency, sodium vapor effects on ion gages, and a vacuum analysis with an omegatron-type mass spectrometer are each discussed. (Authors)

E. A. Richley, R. J. Cybulski and T. A. Keller, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 16

57. Performance Criteria for Sorption Pumps. *United States.*

This paper presents data which help to predict the performance of refrigerated sorption pumps under various conditions. By mass spectrographic analysis, it is shown that the residual atmosphere after sorption-pumping of air consists mainly of neon. This result is consistent with separately determined adsorption isotherms of nitrogen, neon and helium. The use of adsorption isotherms and operating lines for predicting the pumpdown of systems by refrigerated sorption pumps is illustrated. Applications to multistage sorption pumping and the use of sorption pumps in conjunction with other vacuum pumps (e.g. mechanical or sputter-ion) are discussed. The important properties of sorbents are listed. (Authors)

F. T. Turner and M. Feinleib, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21

58. A Magnetically Suspended Molecular Pump. *United States.*

The alloy steel rotor of a bakeable molecular pump is magnetically suspended inside a stainless steel vacuum chamber and spun by a rotating magnetic field. Operational data will be given which includes ratios of the pressure on the high side to the low side of the pump as a function of rotor speed and clearance between rotor and stator. Pumping speeds of the order of 10 l/sec, pressures of 4×10^{-10} Torr, and pressure ratios of 10^5 have been obtained. The experimental data will be compared with a theory worked out for the pump. (Authors)

C. E. Williams and J. W. Beams, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21

59. Power Requirements of Oil Sealed Mechanical Pumps.

The power consumption of oil-sealed mechanical pumps will be found to peak in the 200–300 Torr range. A thermodynamic analysis, assuming constant capacity and polytropic compression ($p.v^n$ = constant), locates the lower peak at a compression ratio of $n^{n/(n-1)}$. This expression yields values which agree with observations. A second order approximation was made, taking the variable pumping speed into account. The change in the above expression for the compression ratio was negligible. Measurements made on a series of single stage pumps showed the peak power to be proportional to capacity and in reasonable agreement with theoretical calculations. (Author)

E. A. Winzenberger, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 25

60. Testing Performance of Diffusion Pumps.

Measurement techniques and experimental results are presented for the major performance criteria of oil diffusion pumps. Special emphasis is placed on new developments including the new diffusion pump oils and zeolite traps. Statistical variations observed in testing groups of pumps of the same design are presented. (Authors)

M. H. Hablanian and H. A. Steinherz, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 20 : 32

61. Experience with the Vacuum Equipment for the CERN 25 GeV Proton-Synchrotron. *Liechtenstein.*

The basic conception of the vacuum equipment was that of completely independent pumping units, fully protected and automatically controlled as being almost necessary because of the extended size of the synchrotron. The pumping units and their control system is described in detail. Statistics of test results are represented. Review of over a year's operational experience is given with a brief account of problems encountered. Operational time lost due to faults in the vacuum equipment has proved to be negligible. (Authors)

G. L. Munday and G. Zinsmeister, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 20 : 25 : 32

62. Ring Magnet Vacuum Pumping System for the Argonne National Laboratory Zero Gradient Synchrotron. *United States.*

The Ring Magnet Vacuum Pumping System consists of sixteen 32 in. oil diffusion pumps, modified by expanding the pump casing to accommodate a 48 in. diameter "Z" type chevron baffle, mechanically refrigerated. Outgassing data and high impedance characteristics for the "Spacemetal" inner chamber (average pressure 2×10^{-6} Torr) coupled with a restriction of pumping locations preclude the description of the differential pumping system, pump down procedure, operational controls and protective devices. Two closed ring piping manifolds for the vacuum system, operating as common headers for the pumps, permit the interchangeability of equipment, performance reliability and sufficient flexibility to conform to accelerator operation. (Authors)

R. Trcka and J. Moenich, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 20

63. Aspects of the Technology of Mercury Vapour Pumping Systems. *United Kingdom.*

The performance characteristics of a pumping group employing a mercury diffusion pump are sensitive to factors which are relatively unimportant when an oil pump is used. Among these factors are: the mercury vapour barrier in and above the pump mouth, the surface condition of the pump condensing

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walls, the back migration rate of mercury to the cold trap, the effectiveness for condensing mercury vapour of the trapping surfaces. These factors are discussed in their relationship to equipment design and working conditions. The discussion is illustrated with practical results. (Authors)

B. D. Power, N. T. M. Dennis and D. J. Crawley, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 25 : 23

64. Experiences with Demountable Ultra-high Vacuum Systems. *United States.*

Various ultra-high vacuum pumping groups, based on oil and mercury diffusion pumps and cold traps ranging from 2¼ to 12 in. nominal bore, have been assembled and tested in the authors' laboratory during the last 2 years. The paper summarizes practical experiences and presents practical results. Topics discussed include degassing rates of baked surfaces, new gasketing methods, experiences with a new pumping fluid, new methods of feeding cold traps and ultimates achieved after various histories and with different cold baffle temperatures. (Authors)

B. D. Power and F. C. Robson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 11 : 20 : 32

65. On an Oil Self-purifying Diffusion Pump System. *Japan.*

A special oil diffusion pump system is tested in which two well fractionating pumps are used in series and vacuum pipe lines are specially designed. In the system, impurities of diffusion pump oils are quickly removed and we get a good vacuum with no refrigerated trap and the back-streaming of oils are extremely suppressed. Using this system, our 63 in. variable energy cyclotron is operated with no refrigerated trap, getting good vacuum and great stability. The system is also applied for a pumped klystron using an oxide cathode and the life of the cathode is longer than 500 hr. (Author)

H. Kumagai, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 20

66. Ultra-high Vacuum Pump Sets. *Germany.*

Ultra-high vacuum pump sets can be produced now on a production line and experiences obtained so far will be presented. The various components which make up the complete set and their arrangement are described and also the electronic control gear which includes an interlocking system and appropriate safety devices. Pumping down curves are shown as obtained from a number of identical sets and it will be shown how the general principles of ultra-high vacuum technology have to be applied to practical devices where pressures of less than 10^{-8} Torr have to be obtained and maintained over longer periods of operation. (Author)

H. Adam, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 20 : 18

67. One Year of Operating Experience with Seventy Getter-Ion Pumps. *United States.*

The projected vacuum system for the 30 BeV alternating gradient synchrotron at Brookhaven National Laboratory was outlined at the American Vacuum Society Symposium in 1957 and at the Namur International Congress in 1958. This project, now a reality, has been in operation for more than one year. The operating and maintenance experience on a system using over seventy getter-ion pumps will be discussed. Down-time, component life, technician training, remote control and operation will be features of the talk. (Authors)

C. L. Gould and R. A. Dryden, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 18

68. Some Experimental Data on Parameter Variations with the Triode Ion Pump. *United States.*

This paper will describe briefly the principle of operation of the triode cold-cathode getter-ion pump and present experimental data showing the effects of variations in voltage and magnetic field on pumping speed. Also a series of experiments will be described in which electrode potentials have been adjusted to simulate various diode and triode pump configurations. Mass spectrographic data will be presented, comparing the pumping efficiency and re-emission of various gases when sputter cathodes of titanium, tantalum, zirconium and niobium are used. (Author)

A. R. Hamilton, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21

69. Progress on Optimization of Oil Diffusion Pump Systems for Ultra-high Vacuum—III. *United States.*

New boiler and top jet designs are presented for use with the ultralow-vapor-pressure oils for diffusion pumps reported earlier by Hickman. The boiler design has unique features : (1) It eliminates eruptive boiling, (2) creates superheated vapor at 300°C and maintains liquid oil below 100°C, (3) starts and stops producing a vapor stream in 5 sec, (4) permits air to be introduced without damage. The new jet design provides high vapor density, yielding Ho factors >0.85 for nitrogen and a fore pressure tolerance >1 Torr. Overall pump height can be numerically smaller than the diameter of the top of the pump. (Authors)

N. Milleron and L. L. Levenson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 54

70. Evaluation of a High-temperature Functional Fluid in a Conventional Diffusion Pumping System. *United States.*

A high temperature fluid " Monsanto OS-124 " was tested in a PMC 720 diffusion pump. The fluid was evaluated on the basis of its performance in a conventional system with a few simple modifications. The effects of variations in the boiler input and pump barrel temperature were noted. The base pressure and speed with a one bounce baffle operated at various temperatures were checked. The composition of the residual gas at the base pressure was determined with a mass spectrograph. And of great importance to the Sherwood Project, the effect on the fluid of a large hydrogen throughput was checked. (Author)

T. H. Batzer, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21

71. Cryopumping for Ultra-high Vacuums. *United States.*

Theoretical considerations of the gas flow-condensation and heat transfer phenomena for radiation-shielded condensing surfaces, operating in the free-molecule flow regime are reviewed; important and useful parameters relating to typical cryopumping geometries are defined and discussed. Experimental results, including gas pumping rates and heat loads from tests on a particular geometry mounted within a 3 ft diameter $\times$ 4 ft long cylindrical high vacuum chamber are described. Experimental results are compared to those derived from theory. (Author)

R. W. Moore, Jr., *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 17 : 52

72. A Catalytic Method for Cryopumping Hydrogen. *United States.*

Experiments were conducted to examine the feasibility of cryopumping hydrogen by means of an intermediate catalytic

surface reaction. Hydrogen was reacted with oxygen *in vacuo* on a palladium-coated alumina catalyst. The water vapor formed by this reaction was condensed on a liquid-nitrogen-cooled surface. Cryopumping was observed at pressures as low as about 0.4 microns of mercury. The application of this method of pumping to the design of vacuum chambers for testing electric thermal rockets using hydrogen propellant with throughputs of the order of 6×10^6 μl/sec is discussed. (Author)

J. Grobman, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 11 : 18

73. Preliminary Pumping Results with Penning-type Discharges Supported on Condensable Metal Vapors. *United States.*
A Penning discharge, supported on a pseudo gas of metal vapor, functions as an ion-getter pump. Liquid metal that is molten at 60°C and has vapor pressure less than 10^{-12} Torr is used as cathode material ; it is vaporized continuously by a tungsten wick. This metallic vapor, condensable within line of sight, is used to sustain a Penning discharge at constant current independent of diminishing gas pressure outside the discharge. The pumping effect observed with this metallic vapor-supported discharge is attributed to interaction between ions and the liquid cathodes. Energetic beams of ions or neutrals may be caught by liquid metal targets. (Author)

N. Milleron, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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21 : 22 : 18 : 11

74. Pressure-versus-Time Variation in Closed Vessels Exhausted by Ionic Pumping. *Roumania.*
An equation correctly representing the nonexponential variation of pressure vs. time is obtained, for the case of pumping with an Bayard–Alpert gauge or a Hall pump, or during recovery. Besides other parameters, the adsorption and desorption phenomena occurring on the surface of the vessel, independently of the action of the ionic pump are taken into account too. The experimentally found parameters of the equation permit the determination of the pumping speed and also allow us to draw interesting conclusions as to the adsorption and desorption coefficients, as well as to the quantity of adsorbed gases. (Authors)

G. Comsa and B. Iosifescu, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 20 : 16

75. A Large-scale Getter Pumping Experiment Using Vapor Deposited Titanium Films. *United States.*
The use of titanium getter pumping for large vacuum systems is described. Techniques have been developed which give sorption rates approaching the maximum theoretically possible for many of the chemically active gases. A simple method of determining sticking fractions is described. Sticking fractions for hydrogen, deuterium, oxygen, nitrogen, carbon monoxide, carbon dioxide and methane are given for various films. The capacity and sorption characteristics for these films are shown. Simple and reliable resistance-heated titanium evaporators are described. It has been demonstrated that the pumping methods described provide outstanding performance and are both reliable and practical. (Author)

R. E. Clausing, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

21 : 37

76. Pump for Circulating Gases.
Note by J. Hume, *J. Sci. Instrum.*, **36**, August, 1959, 375.

21 : 12 : 21

Pressure Measurement in Non-baked Ultra-high Vacuum Systems. See Abstr. No. 8.

21 : 16

Some Low Pressure Sorption Characteristics of Evaporated Titanium and Zirconium with Dry Air and Oxygen. See Abstr. No. 35.

21 : 34 : 20

A High-Vacuum Orbital Simulator. See Abstr. No. 178.

21 : 34 : 20 : 17

Space Thermal Environment Simulation Facilities. See Abstr. No. 179.

21 : 34 : 20 : 17

Design and Operating Criteria for Environmental Vacuum Chambers. See Abstr. No. 180.

21 : 47

Pumps as a Gas Source. See Abstr. No. 185.

21 : 11

A Hypothesis Concerning Limitations of Diffusion Pumps. See Abstr. No. 3.

21 : 11 : 16 : 20

Barium Absorption Pumps. See Abstr. No. 5.

21 : 12

Response Time of Thermal Conductivity Vacuum Gauges. See Abstr. No. 15.

21 : 20 : 22 : 33 : 40

A Portable High Speed Ultra-high Vacuum System. See Abstr. No. 45.

21 : 20 : 18 : 28 : 33

A Large Differential Pumping System. See Abstr. No. 46.

21 : 20 : 32 : 24

Ultra-high Vacuum System for a Large Electromagnetic Isotope Separator. See Abstr. No. 50.

21 : 30 : 20 : 22 : 23 : 24 : 25 : 47

A Low Pressure Evaporation Plant for Rapid Operation. See Abstr. No. 147.

21 : 42 : 27

The Use of Semiconductors in High Vacuum. See Abstr. No. 205.

22. Gauges

22 : 12

77. General Observations on Hot Filament Ion Gauge Operation in Homogeneous Magnetic Fields. *United States.*
Ion gauge operation in magnetic fields is sometimes unavoidable. Bayard–Alpert type, high pressure, and conventional ion gauges were operated in a homogeneous static magnetic field of 0.2 Wb/m^2, and in pulsed fields as high as 1.5 Wb/m^2 in several orientations. The effect of the magnetic field on ion and emission currents was noted and compared with that expected from qualitative theoretical considerations. Satisfactory agreement was found. Operation is feasible with proper orientation. (Author)

G. D. Martin, Jr., *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 12

78. A Vacuum Manometer Using Ultraviolet Light.
An ultra-high vacuum manometer which theoretically may measure vacua to better than 10^{-13} Torr is discussed. The device uses a special Geiger-Muller counter tube. This tube counts ultraviolet photons from the electron bombarded rest gas. The device is also a gas analyser when equipped with a set of narrow band ultraviolet transmission filters. The device was tested successfully as a hydrogen leak detector. Theoretical calculations, experimental results, and references are presented. (Author)

I. Alexeff, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 12

79. Further Developments in the Hot-Cathode Magnetron Ionization Gauge. *United States.*
A hot-cathode magnetron ionization gauge capable of measuring pressures as low as 10^{-14} Torr was described at the 1960 AVS Meeting. The low pressure limit of this gauge has been extended by the addition of an electrostatic lens system that focuses the ions on the first dynode of an electron multiplier. This has resulted in further reduction of the X-ray photocurrent and an increase in output current. Photoelectric emission caused by light from the hot filament is reduced by the use of a lanthanum boride cathode which operates at 675°C. Measurements of sensitivity and X-ray photocurrent indicate that this arrangement should have a linear response down to pressures of 10^{-15} Torr with an output current of the order of 10^{-11} A. (Author)

J. M. Lafferty, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 12

80. A Bayard–Alpert Type Ionization Gauge with a Low X-ray Limit. *Netherlands.*
An ionization gauge for ultra-high vacuum work is described. The X-ray limit of this gauge has been lowered by increasing the sensitivity of the gauge for low energy electrons and by reducing the absorption of X-rays by the ion collector wire. It is shown that this can be achieved by choosing a special grid structure and by applying a proper potential distribution inside the grid volume. The X-ray limit of such a gauge will be about $6–10^{10}$ Torr. (Author)

A. van Oostrom, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 12

81. An Ionization Gauge for the Measurement of Ultra-high Vacua. *Germany.*
A hot cathode ionization gauge with an electrode structure similar to that of an omegatron is described. The ionizing electron beam is focused by an axial magnetic field. The electrons traverse the ionization chamber and are finally collected at a trap outside the ionization chamber. The ion collector is arranged inside the ionization chamber at a place where it cannot be hit by X-rays emitted from the electron trap. All ions formed by the electron beam inside the ionization chamber move to the ion collector under the influence of an applied electrostatic field. At pressures lower than 10^{-2} Torr a linear relationship exists between pressure and ion current. The low pressure limit could not be determined up to now. Down to 10^{-11} Torr no indication of a limitation has been found. (Author)

A. Klopfer, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 12

82. H^+_3 and H_2D^+ Ions in the Omegatron. *Roumania.*
The appearance of an unusually large H^+_3 ion current in an omegatron, drowning the HD^+ current at low deuterium concentrations, at 10^{-4}–10^{-7} Torr hydrogen pressures, is discussed. An experimentally checked relation is presented

$$I_{H^+_3} = \frac{2p^2_{H_2}}{A}\left[\sqrt{\left(1 + \frac{A\,\mathcal{J}_{H^+_3}\,k}{p_{H_2}}\right)} - 1\right] \exp\left(-b_{H^+_3}\,p\right)$$

where A, $\mathcal{J}_{H^+_3}$ and K are constants, p_{H_2} the hydrogen pressure and p the total pressure. The high yield of H^+_3 ion formation in the omegatron suggested the idea of detecting small deuterium concentrations by measuring the current of H_2D^+ ions, which appear at least in three different collision processes. Deuterium can be detected down to natural concentrations and even lower ones. (Authors)

G. Bajou and G. Comsa, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 12

83. A Comparison of the Partial-preserve Meters Topatron and Omegatron.
The topatron, a high-frequency spectrometer with a range from 10^{-3} to 10^{-7} Torr, and the omegatron, with a range from 10^{-5} to 10^{-11} Torr, supplement one another in application. Measurements were made which demonstrated the interdependence between the solvent strength and the sensitivity of both instruments. Measures for avoiding disturbances due to background effects are discussed together with harmony relations. (Authors)

G. Reich and H. G. Noller, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 18

84. The " Secondary " Electrical Gas Cleanup Mechanism. *United Kingdom.*
Evidence in favour of a " secondary " cleanup of gas in the hot cathode ionization gauge is reviewed. Experiments are described in which the spontaneous recovery of previously pumped gas is observed. It is found that (1) the gas recovered in this way cannot be pumped and recovered in a reversible manner and (2) gas so recovered is pumped away much more rapidly than one would expect from the initial pumpdown. It is suggested that the secondary cleanup is due to the annealing out of point defect lattice damage caused by the well-known primary cleanup. (Author)

F. A. Baker, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 27 : 37 : 40 : 51

85. Residual Gases in Metal Vacuum System. *Japan.*
The mass spectrometrical investigation of residual gases in a stainless steel mass spectrometer, evacuated with a Pi-ion pump, was carried out. Ion current down to 1×10^{-19} A could be detected with a Cu–Be electron multiplier followed by a vibrating reed electrometer. The results so far obtained are : (1) Main residual gases are found to be H_2 and N_2 (or CO). The partial pressures of these gases are about 10^{-8} Torr. (2) H_2O and Ar have the partial pressure one order of magnitude smaller than that of H_2. (3) Other small components ($<10^{-10}$ Torr) may be attributed mainly to hydrocarbon. (4) $(Ar)/(N_2 + CO)$ ratio is about ten times greater than that when oil diffusion pumps are used. (Authors)

M. Michijima, J. Okano, A. Fujinaga and K. Ogata, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 27 : 37 : 40 : 51

86. Mass-Spectrometer Investigations in Ultra-high Vacuum Systems. *Liechenstein.*
A mass-spectrometer that works on the principle of crossed electrical and magnetic fields—as devised by Bleakney and Hipple—is described. The spectrometer is bakeable and is intended for analysing the composition of the residual-gas

atmosphere in ultra-high vacuum systems. The residual-gas atmosphere in ultra-high vacuum systems, operated with oil-diffusion pumps, was studied with the aid of this mass-spectrometer in relation to the type and temperature of the cathode used. The mass-spectra obtained are discussed. (Authors)

W. K. Huber and E. A. Trendelenburg, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22 : 12 : 18

87. The Mass Filter Partial-pressure Vacuum Gauge. *Germany.* A description is given of the construction and properties of a partial-pressure vacuum gauge which operates on the principle of the so-called mass filter. By the selection of suitably adapted ion sources the measuring cell can be employed in a pressure range extending from a maximum of 5×10^{-3} to approximately 10^{-10} Torr. The incorporation of various analyser systems makes possible for the detectable mass numbers an interval of $m = 1$ to 200 with a resolving power of up to $m/\triangle m = 100$. The versatility of the arrangement is illustrated by the fact that it is possible, depending on the cell equipment, to carry out measurements in a range extending from sensitive ultra-high vacuum to the relatively high pressures encountered in numerous technical applications. (Authors)

K.-G. Gunther and W. Hanlein, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

22

88. Air-bubble Micromanometer for Outdoor Use. Note by E. Kovačič, *J. Sci. Instrum.*, **36**, July 1959, 328.

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22 : 12 : 18

Electrical Cleanup in Ionization Gauges. See Abstr. No. 9.

22 : 12

Design Parameters' Influence on M.I.T.-Bayard–Alpert Gauge Sensitivity. See Abstr. No. 10.

22 : 12 : 18

A Precise Method to Determine Pressures in High Vacuum. See Abstr. No. 11.

22 : 12 : 18

The X-ray Limit in Ionization Gauges. See Abstr. No. 12.

22 : 12 : 24

Use of a Standard Orifice in the Calibration of Vacuum Gauges. See Abstr. No. 13.

22 : 12

Absolute Measurement of High Vacuum. See Abstr. No. 14.

22 : 20 : 21 : 33 : 40

A Portable High Speed Ultra-high Vacuum System. See Abstr. No. 45.

22 : 20 : 12 : 25

An Ultra-high Vacuum Gage Calibration System. See Abstr. No. 48.

22 : 21 : 18 : 11

Pressure-versus-Time Variation in Closed Vessels Exhausted by Ionic Pumping. See Abstr. No. 74.

22 : 30 : 20 : 21 : 23 : 24 : 25 : 47

A Low Pressure Evaporation Plant for Rapid Operation. See Abstr. No. 147.

22 : 40 : 27 : 37

Residual Gases During Operation and Life-testing of Power Klystrons. See Abstr. No. 203.

22 : 40 : 27 : 37

Analysis of Gases in an Oil Pumped Vacuum System by Use of an Automatically Controlled Mass Spectrometer. See Abstr. No. 204.

22 : 12

A Serious Error Caused by Mercury Vapour Stream in the Measurement with McLeod Gauge in the Cold Trap System. See Abstr. No. 6.

22 : 12

Accurate Calibration of Vacuum Gauges to 10^{-9} Torr. See Abstr. No. 7.

22 : 12 : 21

Pressure Measurement in Non-baked Ultra-high Vacuum Systems. See Abstr. No. 8.

23. Plumbing

23

89. High and Low Temperature Vacuum Seals. *United States.* Two types of epoxy vacuum seals have been prepared and used successfully. One type was for use at high temperatures (in a system up to 850°K) and a vacuum down to 10^{-5} Torr. One such seal with six continuous potential leads and two continuous thermocouple leads has been used for several temperature cycles. The second type of seal was prepared from a low temperature variety of epoxy for use at liquid helium temperatures. Several seals of this type have been used up to 1°K and down to a vacuum of 10^{-7} Torr. (Author)

K. S. Balain, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

23

90. Metal-to-Metal and Ceramics-to-Metal Bakeable Vacuum Seals. *Roumania.* Two methods are described for the construction of vacuum-tight and bakeable metal-to-metal and ceramics-to-metal seals, soldered together with aluminium gaskets. The metal-to-metal seals are lighter, smaller and cheaper than the usual flange seals with metal gaskets. They can be easily taken apart. The soldered parts may be of steel, stainless-steel, copper, titanium, etc. Titanium with stainless-steel is described. Ceramics-to-metal seals for insulated terminals may be achieved without complicated technical means, using the same soldered aluminium gaskets. (Authors)

G. Comsa, S. Lungu and C. Simionescu, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

23

91. New Developments in Vacuum Sealing. *United States.* New data concerning efficacy of elastomeric seals in vacuum are presented. Leak rate data and sublimation effects are used to assess the utility of these seals in " ultra high " vacuum systems, and in space. Systems operating at pressures greater than 1×10^{-6} Torr are shown to be independent of elastomer sublimation. Sublimation rates of polymers are discussed. Utilization of microtime specimens is described. Leak rates at several temperatures, permeability, sublimation effects, outgassing, and accessibility are discussed. These limitations are reviewed with

reference to systems with finite pumping capacities and space with its infinite vacuum sink. Optimum seal designs are then developed. (Author)

J. R. Jordan, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

23

92. Ultra-high Vacuum Flanges. *United States.*
A study has been made of the performance characteristics of four leading designs of all-metal flange seals. The aim was to determine which of the designs offered the best combination of performance, reliability, convenience of use, and practical manufacture. Data are presented on leak rate, sealing life, bakeout to 880°C, resistance to mechanical damage, technique of use, and corollary information. Analyses of the sealing mechanism are also presented to explain the differences in performance. (Authors)

W. R. Wheeler and M. A. Carlson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

23 : 27

93. Correlations Between Leak Rate and Some Phenomena Observed in Metal-to-Metal Contact. *France.*
Correlations between the leak rate and phenomena observed in metal-to-metal contact are investigated using a cylindrical ring placed between two flanges. To obtain a leak rate of less than 10^{-10} atm cm^3 sec^{-1}, the required crushing-stress must correspond at least to the yield strength of the cold-worked material. Moreover, there seems to exist a connexion between this required force and the electrical contact resistance. The results are applied to the design of metallic vacuum gaskets. (Authors)

G. Armand, J. Lapujoulade and J. Paigné, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

23

94. A Dismountable Vacuum Joint for Bakeable Glass Systems. *United Kingdom.* Describes a joint in which a metal gasket can be used between glass tubes without the need for a metal flange ; the area of metal surface exposed to the gas in the system is thus kept to a minimum. The joint is based on a type made commercially for joining sections of glass pipeline. A butt joint is made between two glass tubes of the same diameter by compressing a wire ring between the ground ends of the tubes. The outside diameter of each tube increases towards the end and the outer wall is ground to an accurate taper ; a steel flange, fitted over the tube, has an insert of graphite-impregnated asbestos cut to fit accurately to the taper of the glass. The axial force to compress the wire ring between two tubes is then applied by means of bolts running between the flanges on the tubes. There is a sketch of a joint between 2-in. diameter tubes, using a gasket of lead wire (1/16 in. diameter). With a 30 l/sec oil pump and a system volume of 10 l., pressures of 10^{-6} Torr were obtained without baking and of a few times 10^{-7} Torr after baking. For baking temperatures above 300°C, a lead–thallium alloy is suggested for the gasket ; for much lower temperatures, indium could be used.

Note by L. A. Green, H. T. Miles and A. C. Richardson, *J. Sci. Instrum.*, **36**, July 1959, 324-325.

23 : 24

Commercial Seals as Seats in a Bakeable Valve. See Abstr. No. 95.

23 : 21 : 25

Experiences with Demountable Ultra-high Vacuum Systems. See Abstr. No. 64.

23 : 30 : 20 : 21 : 22 : 24 : 25 : 47

A Low Pressure Evaporation Plant for Rapid Operation. See Abstr. No. 147.

24. Valves

24 : 23

95. Commercial Seals as Seats in a Bakeable Valve. *United States.*
A simple bellows-sealed 3 in. valve is described which is based on the commercially available " Marman Conoseal " tube joint for the gate seat. The application is evaluated and valve operating characteristics are given, for the test valve which gave leakage conductances of 10^{-6}–10^{-10} atm cm^3/sec for air. (Author)

J. R. Ullman, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

24

96. Techniques for the Admission of High Purity Gases to a Vacuum System. *United States.*
Techniques for introducing high purity gases into vacuum systems have been investigated with the aid of a bakeable mass spectrometer. When spectroscopically pure gases in glass containers are admitted through break-off tips and bakeable metal valves, impurities have been observed to be introduced. The selective permeation of certain gases through solid membranes has been found to provide gas of high purity. This technique is useful for the admission of oxygen, helium and hydrogen through membranes of silver, silica and palladium or nickel respectively. Results obtained indicate the usefulness of the selective permeation method for gas handling systems for high vacuum work. (Authors)

J. R. Young and N. R. Whetten, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

24

97. Cap-and-cup Mercury Vacuum Seal.
Note by A. J. Gaunt and R. A. Redford, *J. Sci. Instrum.*, **36**, August 1959, 377.

24

98. All-metal High-conductance Vacuum Tap.
United Kingdom. The design uses a modification of the type of seal developed by Alpert and uses a polished stainless-steel spherical plunger forced via a bellows into a soft copper annulus. The tap has two inlet ports at right angles. Leakage is claimed to be less than 10^{-7} l.mb/sec. The taps in use have been baked at 250°C, the moving parts being lubricated with molybdenum disulphide.

Note by A. Crocker, *J. Sci. Instrum.*, **36**, October 1959, 447.

24 : 37

99. Device for Admitting Gas at Constant Rate to Vacuum Apparatus.
Canada. A semi-automatic device for admitting gas at a constant rate to a vacuum system. It resembles a Sprengel pump working in reverse, the gas being carried from a reservoir to the system inlet trapped between drops of mercury falling down a vertical capillary tube. The gas flow is metered by a photoelectric device which counts the drops of mercury as they fall.

Note by A. D. Osborne, *J. Sci. Instrum.*, **36**, August 1959, 370–371.

24 : 12 : 22

Use of a Standard Orifice in the Calibration of Vacuum Gauges. See Abstr. No. 13.

24 : 12 : 15

Improving the Accuracy of Metering Gas Flow and Computing Throughput. See Abstr. No. 18.

24 : 20 : 32 : 21

Ultra-High Vacuum System for a large Electromagnetic Isotope Separator. See Abstr. No. 50.

24 : 30 : 20 : 21 : 22 : 23 : 25 : 47

A Low Pressure Evaporation Plant for Rapid Operation. See Abstr. No. 147.

24 : 33 : 20

An Ultra-high Vacuum System for Low Energy Electron Diffraction Studies. See Abstr. No. 170.

25. Baffles Traps and Refrigeration Equipment

25

100. An Efficient In-line Combination Liquid Nitrogen Cold Trap and Refrigerated Baffle for Use on Mercury Pumped Ultra-high Vacuum Systems. *United States.*

A combination liquid nitrogen cold trap and refrigerated baffle has been designed for use with mercury diffusion pumps on ultra-high vacuum systems. This compact all stainless steel unit features high trapping efficiency and economical operation. Optical density is assured although inlet and outlet connexions are in line. A re-entrant configuration enables the cold trap to retain trapped material despite liquid nitrogen level changes. Mechanical refrigeration of a chevron type baffle permits extended standby operation. Special attention has been devoted to allowing for the non-wetting property of mercury.

(Authors)

T. Foote and D. Damoth, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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25 : 16

101. Mechanism and Properties of a New Device to Reduce Back-streaming of Hydro-carbon Molecules. *Liechtenstein.*

The ion baffle is a device to reduce the back-streaming of hydrocarbons. It consists of a cold cathode gas discharge arrangement of the magnetron or inverse magnetron type. It is essentially based on (1) transforming the hydrocarbon molecules into a solid polymer by ion impact, (2) the absorption of gas or vapour molecules in the layer of polymer. The mechanism of the polymerization by ion as well as electron impact is treated theoretically and verified by experimental results. With the ion baffle the hydrocarbon content of the residual gas atmosphere, e.g. from rotary oil pumps, can be reduced to about 1 per cent of its original value. With oil diffusion pumps at total pressures $<10^{-5}$ Torr it is useful that an additional source of current carriers in the ion baffle is brought into operation.

(Author)

R. A. Haefer, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

25 : 16

102. Adsorption Capacities of Some Room-temperature Trap Materials. *United States.*

This work presents some results obtained with a 10 in. dia. room-temperature isolation trap above a 7 in. oil diffusion pump. The trap material was artificial zeolite. The pump fluid was Convoil "20". After bakeout the fine pressure was 2×10^{-9} Torr at an ambient temperature of 21°C. Cooling the trap with liquid nitrogen caused the pressure to fall to 4×10^{-10} Torr. Hydrogen, helium, argon, nitrogen, carbon monoxide, carbon dioxide, methane and *n*-butane were each bled into the fine pressure volume with the trap at room temperature to study adsorption. Adsorption was observed for only CO_2 and *n*-butane. With the trap at room temperature, evaporating less than 1 cm^3 of Convoil "20" into the trap caused the fine pressure to rise to 1×10^{-8} Torr.

(Authors)

L. L. Levenson and N. Milleron, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

25

103. Design and Operation of a Two Refrigerants, Two Stage Refrigerating Unit to Produce Temperature of —130°C and its Use on Low Temperature Oil Traps. *Belgium.*

The aim of this work was the construction of a refrigerating unit for diffusion pump baffles and traps. We wanted to obtain, with simple installations, temperatures between −60 and −70°C, and with more elaborate units, temperatures well below −100°C. We discarded the present two stage, one refrigerant plants because of their peculiarity in circulating the lubrication oil from one stage to the other. (We know a type of two stage, one refrigerant unit which would be free from this defect, but to our knowledge this type has not yet been industrially tested.) We chose hermetic units since they are very secure and may be obtained in powers up to 5 h.p. As regards the refrigerants, we limited our investigations to fluorinated hydrocarbons for security reasons. (Author)

R. Servranckx, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

25

104. A Circulating Liquid-nitrogen-cooled Baffle for Ultra-high Vacuum Systems. *United States.*

The development and design of a circulating liquid-nitrogen baffle for bakeable ultra-high vacuum systems is described. Liquid nitrogen is circulated through a spiral tube that is brazed to a copper baffle barrel. This assembly is in turn contained in a stainless steel vacuum jacket. The baffle and circulating system was designed for a complex ultra-high vacuum system requiring eleven diffusion pumps. A 4 in. baffle, unbaked, has attained a pressure of 3×10^{-9} Torr; a baked (250°C) 6 in. baffle has attained a pressure of 3×10^{-10} Torr. There is no apparent size limit to this baffle design. (Author)

A. R. Taylor, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

25 : 21 : 40

Low Temperature Cooling Experiments with Ultra-high Vacuum Pumping Units. See Abstr. No. 53.

25 : 20 : 12 : 22

An Ultra-high Vacuum Gage Calibration System. See Abstr. No. 48.

25 : 21 : 20 : 32

Ring Magnet Vacuum Pumping System for the Argonne National Laboratory Zero Gradient Synchrotron. See Abstr. No. 62.

25 : 21 : 23

Experiences with Demountable Ultra-high Vacuum Systems. See Abstr. No. 64.

25 : 21

Testing Performance of Diffusion Pumps. See Abstr. No. 60.

25 : 30 : 20 : 21 : 22 : 23 : 24 : 47

A Low Pressure Evaporation Plant for Rapid Operation. See Abstr. No. 147.

26. Automatic Protective and Control Equipment

26

105. Automatic Constant Level Device for Liquid Air.

Note by J. Flinn and P. Moore, *J. Sci. Instrum.*, **36**, August 1959, 374.

27

106. Production Leak Testing of Large Pressure Vessels. *United States.*

A method and apparatus for dynamic leak measurement of large pressure vessels are described. The method as used in

production has been used on vessels from ½ to 30 cubic feet of volume, having leakage rates from 1×10^{-2} to 2×10^{-6} atm cm³/sec. Techniques and hardware improvements which made this range possible are discussed, as well as the factors which caused them. Some of the sources of error and their elimination are considered. Data are provided indicating the practicality of this method as a production inspection tool for pressure vessels, both large and small. (Author)

J. G. King, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

27

107. High Sensitivity Helium Mass Spectrometer Leak Detection. *United States.*

An experimental high sensitivity helium mass spectrometer leak detection system is described. The instrument incorporates a highly effective ion source, a two-stage analyser tube, and a differentially pumped source region. The minimum-detectable-leak of this system is 5×10^{-13} atm cm³/sec (helium). A new concept, the Sensitivity Figure of Merit, is presented which permits a more complete evaluation of an instrument. (Authors)

M. Doctoroff, S. S. Grossel and D. W. Oblas, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

27 : 14

108. Standard Leaks and Their Calibration by Constant Pressure Change in Volume Techniques.

Standard leaks are calibrated using $p(\triangle V/\triangle t)$. For leakage rates $>10^{-6}$ Torr l/sec a valved off evacuated volume is used for $\triangle V$. For rates in range 10^{-10}–10^{-6} Torr l/sec $\triangle V$ is obtained by the mechanical expansion of metal bellows. The pressure is the same at the beginning and end of the time interval $\triangle t$ for both cases. Because of its nonpumping characteristic, a Knudsen vacuum gauge is used to determine p in the calibration of the slower leaks. Standard leaks having rates of 10^{-6} to faster than 10^{-3} Torr l/sec and normal calibration periods of 12 months are described. (Author)

M. K. Laufer, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

27

109. Leak Detection with Radio-Isotopes.

Report in *Engineer*, **210**, 5459, p. 438, 9 September, 1960.

27 : 20 : 32

Problems Peculiar to Very Large Systems. See Abstr. No. 43.

27 : 22 : 37 : 40 : 51

Residual Gases in Metal Vacuum System. See Abstr. No. 85.

27 : 22 : 37 : 40 : 51

Mass-spectrometer Investigations in Ultra-high Vacuum Systems. See Abstr. No. 86.

27 : 23

Correlations Between Leak Rate and Some Phenomena Observed in Metal-to-Metal Contact. See Abstr. No. 93.

27 : 40 : 22 : 37

Residual Gases During Operation and Life-testing of Power Klystrons. See Abstr. No. 203.

27 : 40 : 37 : 22

Analysis of Gases in an Oil Pumped Vacuum System by Use of an Automatically Controlled Mass Spectrometer. See Abstr. No. 204.

27 : 42 : 21

The Use of Semi-conductors in High Vacuum. See Abstr. No. 205.

28. Heating Equipment

28 : 37 : 45

110. Fusion Welding of Beryllium in a Vacuum Atmosphere. *United States.*

Both hot-rolled and pressed-and-sintered beryllium have been successfully fusion welded utilizing an electron beam as a heating source. It was found that with proper heat input and operating pressure conditions, leak tight beryllium weldments having equivalent tensile strengths in the fusion, heat-affected, and base plate zones could be accomplished. Thus, vaporization and thermal cracking limits for operating vacuum and power input could be defined for a particular specimen and quench block geometry. Repair welding of cracks or voids was not found possible for specimens exposed to air prior to repair welding attempts, presumably because of air entrapment within the crevices. (Authors)

W. I. Hess, H. J. Lander and S. S. White, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

28 : 37 : 30 : 49

111. Contribution to the Problem of Electron Beam Design for Melting, Welding, Evaporation and Drilling Processes. *Switzerland.*

The conditions for electron beams in melting, evaporation, welding and drilling devices are established and some theoretical aspects of beam design for achieving this condition discussed. The properties of thermionic cathodes in this connexion are of great importance in both cases, by achieving high emission current densities and by achieving high emission currents. An effective cathode must be uniform in the emitting surface and equipotential. The operating conditions in such devices limit the selection of cathode materials to a small number. The destroying effect of the positive ion bombardment is very important. This is illustrated by the disturbance of current density in beam-focus (cross over) in a system with a plane tungsten cathode. To overcome the difficulty of positive ion bombardment of the cathode an electron gun system with ion separation has been developed and is discussed in detail. Two types of electron bombardment heated cathodes are described for high power electron guns. The first one is the " Bolzen "-cathode, more suitable for high emission current densities (e.g. 25 A/cm²) and the second one, the disk cathode for high emission currents (e.g. 1 A). The characteristics of this cathode as well as the characteristics of an electron gun with " Bolzen "-cathode and ion separation are discussed. A 25 kV electron beam system for versatile applications is described. The possibility of achieving deep welding by a " medium " high voltage electron beam is illustrated. (Authors)

E. B. Bas, G. Cremosnik and H. Lerch, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

28 : 37

112. Controlled Atmosphere Levitation System.

Australia. Describes part of an equipment for melting and casting small quantities of reactive metals *in vacuo* or inert atmosphere. The specimen to be melted is supported by the high-frequency field of a conical coil with two co-planar, reversed, turns a little way above the cone. To control the rate of heating, the specimen can be made to rise out of the cone (towards a weaker part of the field) or *vice versa* by adjustment of the high-frequency current. The coil system is mounted inside a bell-jar with a turret head which carries the samples and moulds. An alternative system, with a three-section coil, allows small samples to be levitated in a glass tube with the coil outside ; this reduces the volume of the vacuum system to 100 ml. The vacuum and gas admission system is briefly

described. There is reference to the use of gas filling to prevent excessive rise in temperature of the sample and to reduce loss of metal by evaporation. The unit has been used to melt silver, copper, aluminium, iron, silicon, cobalt, nickel, titanium, and zirconium, while graphite has also been levitated to allow it to react with metals. There are six references to other work.

B. Harris and A. E. Jenkins, *J. Sci. Instrum.*, **36**, May 1959, 238–240.

28 : 48

113. A Method of Producing Eddy-current Heating.
Letter from R. J. Armstrong, *J. Sci. Instrum.*, **36**, May 1959, 246.

28 : 30

A Continuously fed Electron Bombarded Source for the Evaporation of Alloys Containing Nickel, Iron or Cobalt. See Abstr. No. 120.

28 : 33 : 45

Electron Beam Welding of High Strength Alloys. See Abstr. No. 166.

28 : 33 : 45

High-power-density Electron Beam Welding of Several Materials. See Abstr. No. 167.

28 : 33 : 45

Electron Beam Processes at Different Voltages. See Abstr. No. 168.

28 : 33 : 45

Studies on Electron-beam Welding. See Abstr. No. 169.

28 : 37

Melt Stock Cathode for Low Voltage Vacuum Melting Furnace. See Abstr. No. 185.

28 : 37

Electron Beam Melting with Multiple Guns. See Abstr. No. 193.

28 : 37

Production Experience with a 5000 lb Vacuum Induction Furnace. See Abstr. No. 194.

28 : 37 : 41

Studies on Vacuum Induction-melting of Iron and Nickel. See Abstr. No. 187.

28 : 37

The Megawatt Class Electron Beam Melting and Casting Furnace. See Abstr. No. 188.

28 : 37

Experience with an Electron Beam Melting Furnace. See Abstr. No. 189.

28 : 20 : 18 : 21 : 33

A Large Differential Pumping System. See Abstr. No. 46.

28 : 30 : 56

Production of Monocrystalline Germanium-films by Electron Beam Evaporation in Ultra-high Vacuum and their Electrical Properties. See Abstr. No. 155.

28 : 37 : 42 : 53

Vacuum Hot Pressing of Refractory Materials. See Abstr. No. 198.

29. Miscellaneous

29

114. An Extruder for Indium.
Note by R. L. Simpkins, *J. Sci. Instrum.*, **36**, July 1959, 327.

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Vacuum Applications

30. Evaporation and Sputtering

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115. Filament Arrangements for Film Thickness Uniformity in Vacuum-deposited Magnetic Thin Films. *United States.*

In order to produce a high grade of magnetic thin films suitable for use in a memory device, it is necessary that the films exhibit uniform thickness and composition distribution over the substrate area. It has previously been established that the configuration of the source filaments has a direct relationship to the thickness uniformity. Therefore, several configurations were designed and calculations were performed to determine which configuration would produce the highest degree of thickness uniformity. This report describes nine configurations designed and the calculated thickness that would be produced by each. (Author)

J. H. Engelman, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 31

116. A Theoretical Method for Calculating Single Coils for Gas-filled Incandescent Lamps.

The equations proposed at Namur for the rate of volatilization are employed for practical purposes. The construction data of single coils of gas-filled lamps are calculated with their help. It is proved that a common length can be found for coils thus calculated for a series of lamps. The extent to which this can be done without affecting the quality of the lamp can also be determined. The life of a lamp at various voltages is calculated with the help of the rate of volatilization and a new method is given for calculating the voltage–lifetime coefficient. (Author)

R. Kövesligethy, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30

117. Evaporation of a Large Amount of Aluminum.

The evaporation of a large amount of aluminum was attained by feeding an aluminum wire against the wall of a graphite boat at the liquid aluminum level. In this way the wire was heated by the radiation from the aluminum pool in the boat during the feeding process, and melted into the pool just as it made contact with the wall. The overflow of the liquid aluminum from the brim of the graphite boat during evaporation was prevented by providing the brim of the boat with an Al_2O_3 barrier in the groove. (Authors)

Y. Moriya, N. Okuma and K. Sugiura, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30

118. An Evaporation Rate Control System Employing a Heated Electrode Sensing Charge. *United States.*

A heated electrode evaporation rate sensing device based on the Bayard–Alpert ionization gauge, is described. With the exception of the sensing device, commercially available components are used for a complete evaporation rate and thickness control system. A discussion of the application of the rate control system in the fabrication of multi-layer devices is presented. Calibration methods and sensing device limitations are discussed. The relative sensitivity of the device for two metals and an insulator is also presented. (Author)

M. H. Perkins, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30

119. The Influence of A.C. on the Evaporation of Tungsten Filaments in Vacuum. *Israel.*

The relation between the evaporation rate and the temperature of the filament is put in an exponential form allowing us to study the influence of the kind of the current on the rate of evaporation. It is deduced that the equation of the temperature fluctuation of a filament heated by a.c. is of sinusoidal form having a frequency double of that of the a.c., and an amplitude that depends on the power consumption of the filament. The author concludes that the influence of the kind of current on evaporation rate is important for filaments with small diameters. (Author)

A. Roth, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 28

120. A Continuously-fed Electron Bombarded Source for the Evaporation of Alloys Containing Nickel, Iron or Cobalt. *United Kingdom.*

The general design of an improved electron bombarded evaporation source is discussed, and the use of this source is investigated for the evaporation of some metals including nickel, iron, cobalt, and some alloys. Provision is made for continuous evaporation by replenishing the source using a wire-feed mechanism. The alloy 80 : 20 nickel–chromium is now of particular interest in the deposition of thin film resistors and micro-circuit elements. The rate of evaporation of this alloy was measured over a range of h.t. power input up to 800 W, and the deposited films were analysed to determine the relative proportion of the two constituents of the alloy. Details of power input, source temperature, rate of evaporation, and separation of the alloy are given. (Authors)

G. Siddall and B. A. Probyn, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30

121. Preparation and Properties of Evaporated Silver Films. *United States.*

Thin silver films in the range of 50–250 Å were prepared by evaporation in vacuum from a tungsten mesh boat on to a clean glass substrate. The resistance of the films per square, the temperature coefficient in vacuum, and the transmission at various wavelengths of light were measured. By measuring the change in electrical resistance, the stability of these films for periods up to several days was determined at several temperatures in vacuum, dry air, argon, and mixtures of O_3, N_2O and H_2O with dry air.

R. T. Galla, R. F. Hoeckelman and C. C. Matle, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 18

122. A New Deposition Technique for Refractory Metal Films. *United States.*

As part of an investigation to produce high-stability corrosion-resistant superconducting films the vacuum-arc process has been modified in such a manner that it may be used in the laboratory for the deposition of high-purity specular refractory metal films. Deposition rates of greater than 50 Å/sec have been obtained for tantalum at a distance of 4 cm from the source. To date, niobium, tantalum, vanadium and iron films have been produced. What is believed to be a new vacuum-arc phenomenon has been observed. (Authors)

M. S. P. Lucas, G. R. Vail, W. C. Stewart and H. A. Owen, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 19

123. Tracer Studies of Vapor-deposited ZnS : Ag Phosphor Films. *United States.*

Studies made with a recently developed nondestructive radioactive-tracer technique in which S^{35} and Ag^{100m} are used to analyse the chemical composition of vapor-deposited films indicate that both the activator and the co-activator atoms in the ZnS : Ag,Cl phosphor tend to fractionate off the host material during high-temperature evaporation and that both the total amount of deposit and activator concentration are strongly affected by the temperature of the substrate. This paper describes method for the preparation of transparent luminescent films and presents general correlation of film composition, film thickness and luminescence efficiency. (Author)

J. K. Lee, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30

124. Production of Thin Self-supporting Carbon Films.

Thin self-supporting carbon films 50–10,000 Å thick and up to 15.5 cm^2 in area were prepared from a carbon arc in an evacuated system. Methods for removing the carbon films from the substrate are discussed. Thicknesses were determined by using a multiple-beam interferometer. (Author)

B. J. Massey, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 51

125. A Stylus Method for Evaluating the Thickness of Thin Films and Substrate Surface Roughness. *United States.*

A stylus method for the determination of the thickness of thin films was compared to weight, interferometric and X-ray methods. The stylus method is a rapid technique for thickness profile evaluation with an accuracy of ± 50 Å in the range from 100 to 10,000 Å. The surface roughness profiles of substrates commonly considered for their film microcircuitry have been determined. The quality of the surface can be described by four arbitrary numbers which attempt to distinguish the average roughness from the maximum roughness. This technique has been used to correlate the electrical properties of tantalum thin film components to surface roughness. (Authors)

N. Schwartz and R. Brown, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 19

126. Instrument for the Controlled Deposition of Optical Film Systems. *United Kingdom.*

The optical thickness of films deposited by evaporation or sputtering in a vacuum coating plant may be controlled by measuring their reflectance or transmittance during deposition. The accurate control of individual film thickness is particularly important when producing multi-layer interference systems. The problems involved in the design of an instrument to meet this requirement are discussed. The construction of a special modulated-beam photometer in which a monitoring light is chopped at 33 c/s and the output from a photocell is amplified by a tuned low-frequency amplifier is described. (Authors)

W. Steckelmacher and J. English, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 19

127. Thickness Determination of Thick Films with Multiple-beam Interferometry.

In multiple-beam interferometric determinations of film thickness, ambiguity of results is sometimes unavoidable if the film sample is a multiple of the half wavelength of the monochromatic light source, and especially if the sample has very small planar dimensions. This ambiguity is eliminated by using a variation of the method of exact fractions. The technique utilizes only two of the powerful mercury characteristic lines, obviates compilation of tables, and does not require an approximate knowledge of film thickness or a knowledge of the direction of line deviation. The initial accuracy of the interferometer is retained. (Author)

S. J. Lins, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 33

128. Electron Microscopy of Glass and Quartz Substrate Surfaces for Thin Films. *United States.*

Soft glass, pyrex, and quartz surfaces exhibit large smooth areas and also localized defects. Individual $6\ \mu \times 9\ \mu$ fields are sometimes quite flat, sometime wavy on a scale of 1–5 μ. Soft glass shows few scratches, but those found are usually severe, indicating accidental scratching. Pyrex and quartz show numerous scratches attributable to polishing, also localized depressions probably due to gouging, and larger very rough areas with no scratches, indicating bowl-like depressions where polishing did not occur. Some discussion of films deposited on these substrates will be presented. (Author)

C. J. Calbick, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

129. Coating Technique in Ultra-high Vacuum.

Coating in vacuum becomes increasingly important for producing electrical components, for example memory elements, semiconductor applications, and micro-miniaturization of circuits. To give exact physical definition of the coating conditions, in order to secure reproducibility and quality of the products, it is essential to perform these manufacturing processes in ultra-high vacuum. In this paper, the technical possibilities of such processes are examined. Our experience will be discussed on the basis of our own experience work. Results about the runoff of the process and specific controls are given. (Author)

J. T. Moll, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 18

130. Sputtering Yields at Medium and Low Energies. *United States.*

Experimental methods of measuring sputtering yields of polycrystalline metal and semiconductor targets under normally incident low and medium energy mercury and noble gas ion bombardment are described. Measurements are made by immersing targets like large Langmuir probes in a low pressure, high density plasma. Notable features of the yield results are discussed with emphasis on recent results at very low ion energies. (Author)

R. V. Stuart, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 18

131. A Theoretical Model of the Sputtering Process. *United States.*

After a brief section devoted to sputtering theories, a semi-quantitative model of the sputtering process is presented in some detail. This model draws upon the older statistical theory, but incorporates important features from the energy-chain mechanism proposed by Silsbee. Qualitatively, the model is consistent with all available sputtering data, and demonstrates why previous quantitative theories have had some limited success. Finally, future theoretical developments and experiments which would clarify the theoretical situation are discussed. (Author)

D. E. Harrison, Jr., *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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30 : 18 : 33

132. Ion Beam Apparatus for the Study of Angular Distribution of Sputtered Material. *United States.*
An apparatus is described for determining the intensity distribution of material sputtered from solid surfaces under heavy ion bombardment at any angle of incidence by means of radioactive tracers. A 10–30 mA/cm² rare gas ion beam is extracted from a modified Von Ardenne source at 1–30 keV and allowed to strike at 1.5 mm diameter radioactive target. Two Mylar collector strips circularly disposed above the target are removed after each run and cut into sections corresponding to 10° angular increments and counted in a NaI well counter. The apparatus can be adapted to produce beams of many different ions. (Author)

R. D. Knight, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 18

133. The Sputtering of Copper by N_2^+ as a Function of Pressure and Temperature. *United States.*
Sputtering yields of copper under bombardment by mass-analysed beams of N_2^+ have been measured at 3 keV as a function of the target chamber background pressure (3×10^{-5}–5×10^{-8} Torr) and the target temperature (60–475°C). A specially designed ultra-high vacuum system made it possible to control the background pressure independently of the beam current. The target temperature at the beam spot was controlled independently of the beam current density. The results are discussed in terms of sputtering mechanisms. (Authors)

T. W. Snouse and M. Bader, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30

134. A Special Evaporator for Reflective Coating of a 74 in. Astronomical Mirror.
For the purposes of the vacuum deposition of aluminum using a special evaporator, a vacuum 1×10^{-5} Torr or less during the evaporation was desirable. This was because of the large distance between source and substrate. A getter pump was obviously a feasible solution to this problem. Additionally, the power source for ion bombardment could also be used for titanium evaporation. An end vacuum less than 1×10^{-6} Torr in the chamber was obtained by using a 20 in. getter chamber backed by a 10 in. diffusion pump and 3000 l/min rotary pump. A satisfactory film was obtained by evaporation at 1×10^{-5} Torr immediately after bombardment had cleaned the substrate. (Authors)

H. Takei, C. Hayashi, H. Mizorogi and Y. Fujino, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 18

135. Physical Sputtering. *United States.*
Experimental facts about physical sputtering at low, medium and high ion bombarding energies are summarized with emphasis on those more recent results which will not be the subject of papers presented in this session. Studies of single crystal sputtering, oblique ion incidence and measurements of sputtered atom velocities all very strongly support a momentum transfer process which resembles a billiard game with atoms. The areas in which sputtering finds increasing interest either as a desirable or undesirable phenomenon are pointed out. (Author)

G. K. Wehner, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 18

136. High Energy Sputtering. *Sweden.*
The sputtering rate varies with the type of bombarding ions and with the target material. In order to study details we have used ions of the noble gases neon, argon, krypton and xenon at energies 5–65 keV and bombarded many different materials. Here the influence on sputtering from ions trapped in the target is very small and therefore it has been possible to arrive at an approximate sputtering equation. One step further has been to measure self sputtering ratios which also suit the same equation. In addition, all ions fit into a systematic trend throughout the periodic system of elements, but it has not hitherto been possible to generalize. (Authors)

O. Almén and G. Bruce, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 53

137. Vacuum Deposition of Ductile Metallic Films. *United States.*
Techniques for preparation of ductile, thin, self-supporting metal films have been developed. The process takes place in a vacuum chamber, using specially designed apparatus for (1) evaporating iron, nickel, cobalt, manganese, chromium and other metals ; and (2) annealing the deposited film. Substrates are carefully coated with a water-soluble film before deposition is started. On completion of the process, the metal film is separated from the substrate by immersion in water. The film is then cleaned, weighed and mounted. (Authors)

W. F. Brunner and H. G. Patton, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 53

138. Vacuum Evaporated Silicon Films.
Vacuum evaporated films of elemental silicon were prepared using a crucible of boron nitride in a carbon resistance heating element. The effect of the quartz substrate temperature, in a range to 1000°C, on the nature of the film was investigated. The electrical resistivity and its temperature coefficient exhibited marked minimal values of 0.02 ohm-cm and -200/°C respectively for substrate temperatures between 600 and 700°C. With increasing substrate temperature the films displayed increasing degrees of (poly)crystallinity by X-ray diffraction, and greater surface roughness by electron micrograph. Post-deposition thermal annealing of the films produced effects similar to varying the substrate temperature. (Author)

F. M. Collins, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

139. The Electrical and Structural Properties of Dielectric Metal Mixtures. *United States.*
A technique is described to evaporate metal-dielectric mixtures from two separate but simultaneously controlled sources. The automation of the deposition rate and substrate temperature controls is presented in detail. The influence of the film composition, substrate temperature, deposition rate and thickness on the structure and resistivity of the deposits has been studied on the following materials : gold–magnesium fluoride, chromium–magnesium fluoride, gold–silicon monoxide, and chromium–silicon monoxide. The results of these measurements, and the influence of annealing cycles and load tests on the stability of the investigated films will be presented in detail. (Authors)

M. Beckerman and R. E. Thun, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

140. Study of the Variation of Dielectrical Properties of Semiconducting Compounds During Evaporation by Means of an Apparatus for Multiple-evaporations in High Vacua. *France.*
We describe an apparatus for multiple-evaporations in high vacua, of the " all metal " design, with a titanium evaporating pump. This apparatus is equipped with a rotating turret monitoring six working glass plates and six monitoring microslides intended to measure the thickness of the dielectric. This equipment allows one to deposit successively on the six plates, by thermal evaporation, superposed layers of metals and of

dielectrics or semiconducting compounds. With this device, we succeeded in showing that the dielectrical properties of the thin layers of certain semiconductors successively prepared, may have depended on the quantity of material already evaporated, and no longer changed from one layer to another after this quantity had become sufficient. (Authors)

R. Guillien, G. Marchal and S. Roizen, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

141. A Method for Detecting Imperfections in Thin Insulating Films.

A simple apparatus has been assembled in which discontinuities occurring in insulating films may be observed in a nondestructive manner. The signal produced by scanning a metal-insulator surface with an electron probe can be used to detect a metal–insulator boundary and also to indicate variations in insulator thickness in the 100–1500 Å range. The usefulness of this instrument in a study of nucleation of molecular beams of insulating materials on metal surfaces has been determined by examining test slides containing various patterns of insulators on a lead surface. While the resolution of the instrument is limited by the radius of the electron beam used, the size of an imperfection which could be detected by the instrument is really dependent only on the current density in the electron beam. Imperfections having an area 1/100 that of the electron beam have been detected without difficulty. (Authors)

E. M. DaSilva and P. White, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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30 : 56

142. Electrical Properties of Metal-dielectric Films. *United States.*

A method for preparing binary composition thin films has been developed which permits determination of the composition of such films. Application of this method to the deposition of composite chromium–silicon monoxide films has indicated the properties of these films are strongly dependent on composition. A model is proposed which considers such films as random mixtures of conductive and insulating particles. The observed electrical properties of the films are in qualitative agreement with this model. (Authors)

W. J. Ostrander and C. W. Lewis, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

143. Evaporated Integrated Microcircuitry for Electronic Systems. *United States.*

The problems in evaporating accurate and stable integrated microcircuits are discussed in detail together with specific solutions. Techniques for producing multiple resistor and capacitor patterns are described. Also discussed are circuit interconnexions, and methods for mounting the evaporated microcircuitry. Methods for inserting unencapsulated transistors and diodes into an evaporated microcircuit are explained. The paper closes with a look at the future of the integrated form of evaporated microcircuitry, with a brief summary of the current status of evaporated single crystal semiconductor films which can ultimately be used to produce evaporated active elements. (Author)

D. W. Moore, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

144. The Deposition of Composite Passive Micro-miniature Circuits by Vacuum Evaporation. *United Kingdom.*

The paper describes a system whereby complete RC circuit networks are evaporated on to a substrate measuring $\frac{1}{2} \times \frac{3}{4}$ in. The resistive elements consist of Nichrome and the dielectric of the capacitors of Silicon Monoxide, while the capacitor electrodes and interconnexions are of aluminium. The depositions are carried out sequentially through accurately-positioned photoetched copper foil masks. The design of the apparatus is such that the masks can be changed readily hence making it a most useful tool in the field of micro-circuit development. (Author)

K. Taylor, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 53

145. Properties of Thin Nickel–Chromium Films. *United States.*

Stable nickel–chromium films of various compositions were deposited in a vacuum by direct sublimation from alloy wires. Composition, thickness and Hall voltage were measured on several specimens. The Hall constant was positive in high chromium films, decreased in value with increasing nickel, reversed in sign at 39 per cent chromium and became increasingly negative as the nickel content increased. The film resistivity was higher than the bulk resistivity. The temperature coefficient of resistance ranged between 5 and 50 p.p.m./°C and was found to depend on film ohms per square. Film stability was found to be excellent. (Author)

T. K. Lakshmanan, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 53

146. Some Properties of Evaporated Refractory Metal Films. *United States.*

Electrical properties of evaporated films of tantalum, tungsten and molybdenum were studied as functions of evaporation conditions and subsequent heat treatment. Temperature coefficients of resistance of tantalum films were always found to be negative and to depend on deposition pressure, substrate temperature and film thickness. The more negative temperature coefficients were associated with the higher resistivities. Heat treatment in air invariably led to negative changes in coefficient and increases in resistivity. Electron microscopy and diffraction studies indicated dependence of film structure on substrate type and exposure of metal to residual atmosphere. The contribution of structural non-uniformity to the temperature coefficient and resistivity is discussed. (Authors)

N. J. Maskalick and C. W. Lewis, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 20 : 21 : 22 : 23 : 24 : 25 : 47

147. A Low Pressure Evaporation Plant for Rapid Operation.

An evaporation plant of the bell jar type is described which has been made for operating in the range 10^{-6}–10^{-8} Torr. The equipment is designed for simplicity of operation and obtains low pressures without baking. The metal bell jar (19 in. dia., 115 l. capacity) is evacuated by a fractionating oil diffusion pump and a Meissner type cold trap placed above the pumping orifice in the vessel. To minimize degassing the high vacuum components are made of stainless steel and the vacuum seals with indium and Viton "A" gaskets. Indium or Viton "A" can be used for the chamber to baseplate seal and the chamber weight is sufficient to make the indium seal without extra compression. Ultimate pressures of 10^{-8} Torr can be obtained after extended pumping or 10^{-7} Torr in 2 hr. When the chamber/baseplate indium seal is replaced by a trapped "O" ring of Buna N or Silastic the ultimate pressure is raised from 3×10^{-8} Torr to about 10^{-6} and 10^{-7} Torr respectively. Gas analysis shows that the water vapour in the residual atmosphere greatly increases with these elastomer seals and nitrogen and oxygen appear in the mass spectrograms. Both elastomers are permeable to the foregoing gases and vapours and the higher ultimate pressures they produce arise mainly from the permeation of permanent gases when the Meissner trap is cooled. (Authors)

L. Holland and S. K. Bateman, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

148. Multilayered Thin Film Capacitors.
The results of statistical studies on the preparation of multilayered thin film capacitors will be presented and discussed. The dielectric material used was silicon-monoxide. Thin films of SiO were vacuum deposited in stacked layers numbering up to 7, separated by aluminum film electrodes, on to supporting substrates of different surface characteristics such as glass, mica and ceramics. Parameters measured and studied include: thickness (interferometrically determined; range for a single dielectric film layer from 1000 to 20,000 Å); capacitance; dissipation factor; leakage current; insulation resistance; dielectric breakdown strength; temperature coefficient; probability distribution for studied parameters. (Authors)

H. J. Degenhart and I. H. Pratt, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56 : 53

149. The Influence of the Deposition Parameters on the Properties of Evaporated Thin Ferromagnetic Films. *United States.*
The magnetic properties of thin films depend on a number of deposition parameters, e.g. type and temperature of the substrate. Gas trapped in the film during its formation is one of the sources of impurities, while oxidation is accelerated by the presence of water vapor in the system. In ultra-high vacuum systems, both residual gas pressure and moisture are greatly reduced. If, in addition, the magnetic measurements are performed *in vacuo*, then one can hope to obtain reliable results. Several examples are given to illustrate the differences between ultra-high and high vacuum depositions. (Author)

K. H. Behrndt, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56 : 53

150. Study of the Magnetization of Ultrathin Evaporated Nickel Films in a Changing Environment. *United States.*
The magnetization of nickel films in the less than 100 Å thickness range was investigated first under ultrahigh vacuum conditions and then after exposure to oxygen or hydrogen at various pressures. Oxidation of the films to a depth of 10–15 Å takes place in a short time even at pressures of oxygen in the 10^{-8} mm range. Exposure to hydrogen of initially clean films resulted only in reversible changes of the transverse anisotropy constant. Unusually large increases in the transverse anisotropy of nickel films result when one goes from a nickel–vacuum interface to a nickel–copper interface. (Author)

C. A. Neugebauer, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56 : 53

151. Stress and Stress Anisotropy in Iron Films. *United States.*
The tensile stress and stress anisotropy in iron films from 200–1000 Å thick were measured at various angles of incidence of the depositing atoms. The ratio of the minimum to maximum stress decreased as the angle of incidence increased. The maximum tension was normal to the plane of incidence. At 36.5°, the stress was about 10^{10} dyn/cm² and decreased with increasing thickness except for a narrow peak at about 700 Å. The stress ratio at 36.5° decreased from 0.94 for a film 216 Å thick to about 0.84 at 700 Å and then increased to 0.89 at 1030 Å. (Authors)

J. D. Finegan and R. W. Hoffman, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

152. Stresses in Evaporated Dielectric Films.
The state of stress of various dielectric films deposited by evaporation has been examined. Stress values have been obtained by observing either optically or electrically the bending of a thin substrate on to which the films were deposited. Dielectric films can show either a compressive or tensile stress. The dependence of these stresses on evaporation and deposition parameters has been examined. It has been shown that these stresses are not usually due to thermal expansion differences between the film and the substrate. The experimental results obtained for different materials are considered in the light of the various theories that have been advanced to explain stress in thin films. (Authors)

H. Blackburn and D. S. Campbell, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56

153. Residual Stress in Silicon Monoxide Films. *United States.*
A study has been made of the residual stress in silicon monoxide films deposited at room temperature. Observed stresses varied from $+16 \times 10^8$ dyn/cm² (tensile) to -5×10^8 dyn/cm² (compressive) depending upon the evaporation conditions. The partial pressure of oxygen present during evaporation and the source temperature were found to influence the residual stress. Significantly, the evaporation parameters may often be chosen such that the residual stress is zero. (Authors)

J. Priest and H. L. Caswell, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56 : 33

154. *In situ* X-ray Diffraction Studies of Thin Film Formation. *United States.*
A vacuum X-ray diffractometer attachment has been developed to observe formation of thin films by vapor deposition or chemical reaction of heated substrates with gases. The apparatus consists of a water-cooled, evacuable compartment, a low-absorption X-ray window, a furnace for heating substrates or samples to 850°C, and two evaporation sources. The sample is aligned by a special slit and an adjustable furnace. The temperature of the substrate is controlled by a current-adjusting controller with a feedback unit, a recorder, and a self-saturating reactor with magnetic amplifier. The apparatus is used to study vacuum deposition of semiconductors on single-crystal substrates and growth of zinc sulfide films by reaction of hydrogen sulfide with zinc surfaces. (Authors)

F. Schossberger and F. Ticulka, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56 : 28

155. Production of Monocrystalline Germanium-films by Electron Beam Evaporation in Ultra-high Vacuum and Their Electrical Properties.
Experiments were made to determine the conditions for the production of polycrystalline and monocrystal line germanium-layers by vacuum-metallization. The layers were deposited in the pressure range of 10^{-5}–10^{-9} Torr on quartz, rocksalt sapphire and single crystal germanium. The evaporation was performed using an electron gun and silica crucibles. The apparatus used and the evaporation process are described. The deposited layers are examined by the Laue back-reflection method and by thermoelectric measurements. (Authors)

W. Reichelt and P. Müller, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 53

156. Preparation and Magnetic Anisotropy of Continuous, Single Crystal Nickel Films. *United Kingdom.*
Thin films of nickel have been grown epitaxially by evaporation on the rock-salt, and their structure determined by electron microscopy. A technique has been developed for the production of continuous films of thickness down to 100 Å. Single crystal nickel films in the thickness range 50–500 Å were prepared and their magnetic anisotropy measured. All films show

an uniaxial anisotropy superposed on the normal cubic anisotropy. In discontinuous films, annealing in vacuum reduces the uniaxial component whilst in continuous films annealing increases it. Films grown in a vacuum of 10^{-7} Torr are found to have few visible imperfections and give more consistent results. The uniaxial component of anisotropy is shown to be a function of thickness, and is affected by the vacuum pressure during deposition. Possible mechanisms are discussed. (Author)

J. C. Anderson, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

30 : 56 : 33

157. Combined Evaporator and Electron Diffraction Apparatus for the Study of Epitaxial Growth. *United States.* A combined evaporator and electron diffraction apparatus is described especially designed for the study of the epitaxial growth of semiconductor films. The main vacuum chamber consists of a stainless steel tube to which the pump, electron gun, sample manipulator, evaporation source assembly and photographic camera are attached. The sample hot stage is mounted to a holder which provides three degrees of freedom for the sample movement. An electron beam energy of 100 kV, a substrate temperature of 1500°C and a final vacuum of 5×10^{-8} Torr can be reached. Results of a study of germanium films epitaxially grown on germanium and calcium fluoride crystals are reported. (Authors)

G. G. Via and R. E. Thun, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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30 : 37

158. Infra-red Absorptiometer, Using Interference Filters, for Analysis of Hydrogen Fluoride in Gaseous Mixtures. *United Kingdom.* A wavelength-scanning infra-red absorptiometer using interference filters has been developed for analysis of hydrogen fluoride in corrosive gases such as uranium hexafluoride. The wavelength scanning is achieved by tilting a narrow-band interference filter of the *etalon* type through a small angle at 10 c/s. This filter consists of a layer of mica with germanium–cryolite–germanium reflectors on each face and has several pass bands about 0.004 μ wide. The tilting causes radiation of two adjacent wavelengths to pass alternately through the same specimen tube ; only one of the wavelengths is absorbed by hydrogen fluoride and the lead sulphide detector receives a steady intensity in the absence of HF. If HF is present, the detector output contains a component at 10 c/s, which is amplified. The instrument is thus independent of corrosion of the windows of the specimen tube, for which polytrifluorchloroethylene has been found to be a suitable material. The prototype instrument detects partial pressures of HF in the range 0.02–20 mm of mercury in 1 atm of the mixture. (Author, modified)

J. A. Harrison and C. D. Reid, *J. Sci. Instrum.*, **36**, May 1959, 240–242.

30 : 49

159. Quick Method of Computing the Transmission of Zinc Sulphide–Magnesium Fluoride Multilayer Filters.
Note by J. E. Knowles, *J. Sci. Instrum.*, **36**, Sept. 1959, 409.

30 : 28 : 37 : 49

Contribution to the Problem of Electron Beam Design for Melting, Welding, Evaporation and Drilling Processes. See Abstr. No. 111.

30 : 37 : 16

The Application of Liquid Metal Circulating Systems in Vacuum Technology. See Abstr. No. 195.

31. Evacuation and Sealing

31 : 30

A Theoretical Method for Calculating Single Coils for Gas-filled Incandescent Lamps. See Abstr. No. 116.

31 : 47

Properties of Modern Barium Getters. See Abstr. No. 208.

31 : 16

Degradation of Glass Vacuum Tubes Resulting from Storage in a Helium Atmosphere. See Abstr. No. 36.

32. Nucleonics

32 : 18

160. Problems Associated with Low Pressure Ion Acceleration. A small sealed ion accelerator neutron source has been developed which, using the deuterium–tritium reaction, produces up to 10^9 neutrons/sec. The tube has been developed for oil well logging purposes where limited amounts of power are available and high ambient temperatures are encountered. The accelerator requires less than 100 W of power and operates at ambient temperatures up to 150°C. The accelerator tube includes the conventional elements of a laboratory accelerator : a gas reservoir, an ion source, an accelerating gap, and a target. The gas reservoir is a zirconium hydride filament and the ion source is a Penning type source. A study has been made of the zirconium hydride system at low pressure and low atomic ratio. All three isotopes of hydrogen have been used in the measurement. A comparison of our results and the data previously published is made. An account of the acceleration of ions at a pressure of 1–20 μ is given. An explanation of the effects observed is given in terms of charge exchange, secondary electron emission, and ionization. (Authors)

A. H. Frentrop and H. Sherman, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

32

161. Alternating Gradient Synchrotron at Brookhaven National Laboratory—No. 1.
Engineer, **210**, 5459, p. 446, 9 September, 1960.

32

162. 4.3 MeV Mobile Linear Accelerator for Weld Inspection.
Report in *Engineer*, **210**, 5472, p. 986, 9 December, 1960.

32

163. Powerful Linear Accelerator for Radiographic Inspection.
Note in *Engineer*, **210**, 5474, p. 1072, 23 December, 1960.

32

164. Alternating Gradient Synchrotron at Brookhaven National Laboratory—No. II.
Engineer, **210**, 5460, p. 481, 16 September, 1960.

32

165. 100 MeV Linear Electron Accelerator for the N.B.S.
Report in *Engineer*, **210**, 5461, p. 519, 23 September, 1960.

32 : 20 : 27

Problems Peculiar to Very Large Systems. See Abstr. No. 43.

32 : 20

Ring Magnet Vacuum Chamber System of the Argonne National Laboratory Zero Gradient Synchrotron. See Abstr. No. 49.

32 : 20 : 21 : 24

Ultra-high Vacuum System for a Large Electromagnetic Isotope Separator. See Abstr. No. 50.

32 : 21 : 20

Experience with the Vacuum Equipment for the CERN 25 GeV Proton-Synchrotron. See Abstr. No. 61.

32 : 21 : 20 : 25

Ring Magnet Vacuum Pumping System for the Argonne National Laboratory Zero Gradient Synchrotron. See Abstr. No. 62.

32 : 21 : 11 : 20

On an Oil Self-purifying Diffusion Pump System. See Abstr. No. 65.

33. General Physics and Electronics

33 : 45 : 28

166. Electron Beam Welding of High Strength Alloys. *United States.*

Five different titanium alloys have been successfully electron beam welded in a variety of fusion zone widths varying from 0.050 to 0.300 in. Impact resistance of fusion zones was compatible with or higher than base plate values, with higher impact resistance evidenced at wider fusion zones. An increase in fusion zone ultimate strength, as compared to that of base plate, was noted. Strength levels correlate with amount of dissolved pre-existing oxide and/or nitride film. Impact resistance is shown to be related to hydrogen content. General ductility losses are reported, but fusion zone elongations, when fractures took place therein, approach those of unwelded material. (Authors)

H. J. Lander, W. T. Hess and S. S. White, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

33 : 45 : 28

167. High-power-density Electron Beam Welding of Several Materials. *United States.*

Electron beam welding studies were conducted with several metallic materials using a Zeiss high voltage high power-density electron beam welding machine. Accelerating voltage, beam current and welding speed were correlated with weld penetration. The effects of material physical properties on welding characteristics also were investigated. Statistical data was obtained for the metallurgical, mechanical and chemical properties of electron beam weldments in materials such as stainless steels, low alloy structural steel, an aluminum alloy, a titanium alloy, tungsten and molybdenum. (Author)

J. W. Meier, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

33 : 45 : 28

168. Electron Beam Processes at Different Voltages. *United States.*

This paper presents the theoretical and experimental results of studies of highly concentrated electron beams operating in a vacuum and at ranges of between 20,000 and 200,000 V. It also offers an analysis of the physics involved in the high and rapid penetration of material possible with this process. For example, an electron beam of 150,000 V and a current of 10 mA can penetrate, within a few seconds, a 1 in. thick stainless steel plate. Special attention is paid to electron optical problems which determine the relation between energy concentration, power (acceleration voltage and current), and electron beam cross section. (Author)

H. Schwarz, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

33 : 45 : 28

169. Studies on Electron-beam Welding. *Japan.*

With an experimental electron-beam welding machine (50 kV × 30 mA, 1.5 kW welding power), effects of welding conditions on welding characteristics such as weld appearance, penetration and soundness of weld were studied with specimens of zirconium, zircalloy-2, titanium, stainless steel, columbium, tantalum and molybdenum. Mechanical properties, microstructures of welded joints and corrosion resistance against high temperature and high pressure water (320°C, 116 atm) were investigated as compared with TIG specimens welded in a controlled atmosphere chamber. (Authors)

G. Itō, H. Susuki, T. Hashimoto and F. Matsuda, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

33 : 20 : 24

170. An Ultra-high Vacuum System for Low Energy Electron Diffraction Studies. *United States.*

An ultra-high vacuum system for low voltage electron diffraction is described and shown schematically and in photographs. This system which uses ion pumps is being used for studying the surfaces of silicon crystals. An integral part of the whole system is a gas admission system by which means gases may be introduced for adsorption studies or for positive ion bombardment of the crystal. In this ultra-high vacuum the crystal surface is stable for days as determined by the diffraction patterns which are observed. Effects due to argon bombardment will also be reported. (Author)

J. Morrison, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

33 : 40 : 37

171. Residual Gases in Closed High Vacuum Systems, Determined by Mass Spectrometry. *United States.*

The use of "static" (closed) vacuum systems has become mandatory in certain geophysical studies, where small gas samples must be conserved. Such work requires vacuum systems that are extremely clean and well degassed, and capable of being baked-out at temperatures of 250–400°C; without sample, such systems must hold at pressures of the order of 10^{-9} Torr. Both glass and metal systems have been used for such work. The systems presently in use will be described, with emphasis on materials, joining techniques, gaskets, valves, getters and pumps, and the residual gas spectra encountered will be described. These mass spectrometer data will be compared with total pressure indications from ion gauges of various kinds. (Authors)

L. F. Herzog, T. J. Eskew and R. L. Erwin, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

33 : 41

172. Surface Structure of Saturated-diode Filaments.

United Kingdom. The life of a tungsten-filament diode when operated from a d.c. filament supply is not necessarily the same as when it is supplied with a.c. Filaments which have been run on d.c. develop a step-like surface structure whereas a.c.-heated filaments become smooth except near the supports. A number of diode filaments have been examined and the results are briefly discussed in this article. (Authors)

F. A. Benson and M. S. Seaman, *Electronic Engng*, **31**, January, 1959, 40–43.

33

173. High Energy, High Current Synchrotron Injector.

G. R. Davies and P. R. Chagnon, *J. Sci. Instrum.*, **36**, July 1959, 306–308.

33

174. Electron-optical Design of an X-ray Microanalyser.

T. Mulvey, *J. Sci. Instrum.*, **36**, August 1959, 350–355.

33

175. Apparatus for Tilting Extraction Replicas Through Large Angles in the Electron Microscope.
Note by G. R. Booker and J. Norbury, *J. Sci. Instrum.*, **36**, August 1959, 368–369.

33

176. Grating Spectrophotometer for the Schumann Ultra-violet Range.
United Kingdom. Constructional and performance details are given of a photoelectric spectrophotometer erected for the measurement of the transmittance of small solid specimens, in the range above 900 Å. The instrument incorporates a one-metre radius, 600 lines/mm Concave grating, and scanning of the spectrum across the exit slit is performed by a linear movement of the centre of the Rowland circle. The mechanical and electrical arrangements permit rapid measurements, quick exchange of specimen and the direct reading of transmittance on a 0–100 scale. There is some description of the vacuum arrangements. (Authors, modified)

F. J. P. Clarke and W. R. S. Garton, *J. Sci. Instrum.*, **36**, September 1959, 403–409.

33 : 18

Positive Ion Bombardment of Metal Surfaces. See Abstr. No. 39.

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Electrical Cleanup by Excitation of Metastable States. See Abstr. No. 40.

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Recent Progress in Vacuum Spectroscopy. See Abstr. No. 42.

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A Portable High Speed Ultra-high Vacuum System. See Abstr. No. 45.

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A Large Differential Pumping System. See Abstr. No. 46.

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Dynamic Pressure Stages for High-pressure/High-vacuum Systems. See Abstr. No. 47.

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Electron Microscopy of Glass and Quartz Substrate Surfaces for Thin Films. See Abstr. No. 128.

33 : 18 : 30

Ion Beam Apparatus for the Study of Angular Distribution of Sputtered Material. See Abstr. No. 132.

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***In situ* X-ray Diffraction Studies of Thin Film Formation.** See Abstr. No. 154.

33 : 30 : 56

Combined Evaporator and Electron Diffraction Apparatus for the Study of Epitaxial Growth. See Abstr. No. 157.

34. High Altitude and Space Technology

33 : 44 : 48

177. Materials Evaluation under High Vacuum and Other Satellite Environmental Conditions. *United States.*
Lockheed Aircraft Corporation, Missiles and Space Division, has an active program on the testing of materials for satellite applications. Among the more important classes being investigated are lubricants and bearings, paints and other temperature control surfaces, bulk plastics and polymer films, and adhesives. Several lubricating oils have withstood over 4000 hr operating time with small, instrument-type ball bearings when tested at 8000 rev/min and 170–180°F bearing housing temperature and 5×10^{-6} Torr. Temperature control surfaces are being irradiated with high intensity radiation in the wavelength range 1100–4000 Å at pressures on the order of 5×10^{-7} Torr. Adhesives and polymers are being subjected to ultraviolet and gamma radiation at elevated temperature. Equipment and data are discussed. (Authors)

P. H. Blackmon, F. J. Clauss, G. E. Ledger and R. E. Mauri, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

34 : 20 : 21

178. A High-Vacuum Orbital Simulator. *United States.*
A high-vacuum orbital simulation chamber is described. The HIVOS chamber is intended as a reliability test facility for the purpose of subjecting complete satellite systems to simulated orbital vacuum and thermal conditions over an extended period. The high vacuum system consists of oil diffusion and diffusion ejector pumps capable of pumping 160,000 l/sec at 1×10^{-6} Torr and attaining an ultimate pressure of 1×10^{-8} Torr or lower in a 5000 ft³ chamber. The chamber can provide both vacuum and radiant flux for a satellite 15 ft in length and 5 ft in diameter. Absorbed fluxes experienced by an orbiting satellite are simulated by use of a quartz lamp-reflector system together with a black thermal sink cooled by liquid nitrogen. The absorbed fluxes can be programmed as functions of time with twenty-six separately-controlled zones. An analog computer programmer is incorporated in the flux control system which utilizes millivolt input signals from twenty-six thermopile radiometers. (Authors)

W. G. Camack and C. A. Ellis, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

34 : 20 : 21 : 17

179. Space Thermal Environment Simulation Facilities. *United States.*
Space Technology Laboratories has constructed two facilities for this aspect of space simulation. These facilities are designed around large vacuum chambers which are used to duplicate the thermal characteristics of the low pressure atmosphere of space. The first thermal simulation facility was initially for evaluation of the Able-5 spacecraft. It is a 7 ft dia., 12 ft long, horizontal cylinder. The second facility is 6 ft in diameter and 10 ft long and is of a Dewar type construction. A high absorptive surface for cryogenic baffles that is compatible with good vacuum technique has been developed. (Authors)

A. D. LeVantine, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

34 : 20 : 21 : 17

180. Design and Operating Criteria for Environmental Vacuum Chambers. *United States.*
The results of designing and operating two environmental vacuum chambers are presented. One 100 ft³ vacuum system at a pressure of 1×10^{-6} Torr was utilized in support of Project Echo, and the other 200 ft³ vacuum system operating at a pressure of 1×10^{-5} Torr supported the Scout Program. Design considerations in heat transfer as they apply to simulating space orbits, the materials of construction utilized, and the results of their application are discussed. The effects of cleanliness, backstreaming, baffling, and the use of cryogenics as they influence pump-down time of both vacuum chambers are presented. (Author)

D. C. Spence, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

34 : 21 : 17

Application of Liquid Helium Cryopumping to Large Electric Rocket Vacuum Facilities. See Abstr. No. 51.

34 : 21

Evacuation Large Space Chambers with Positive Displacement Blowers. See Abstr. No. 52.

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Experimental Evaluation of High-Vacuum Condensers in Large Vacuum Facilities. See Abstr. No. 56.

34 : 54

Biomedical Safety Provisions for Aerospace Environment Facilities. See Abstr. No. 219.

35. Impregnation and Potting

35 : 36

181. High Vacuum Drying and Impregnation Plant for Oil-filled High Voltage Cables up to 500 kV.

A paper-insulated high voltage cable will have the best electric properties if the paper is dried to an equilibrium water vapour pressure of about 10^{-1}–10^{-2} Torr, and if the low-viscous insulating oil is so far dried and degassed that the residual moisture content is less than 1 p.p.m. Avoiding that the non-covered cable during the production process in front of the lead or aluminium press will absorb moisture out of the atmosphere, the cable must be led through a look from the cable tank to the lead or aluminium press. The equipment and process are described which allow drying and impregnation in one process with the impregnated cable directly fed into the lead or aluminium press. (Author)

M. Beyer, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

36. Drying, Degassing and Concentration

36

182. New Experiences in Freeze Drying. *France.*

The process of lyophilization (freeze drying) could not be developed for the manufacture of extensively used foodstuffs because of the high operating costs due to the low speed of the process and the expensive material involved. Experiments on freeze drying made, not in vacuum but in a current of cold and perfectly dry gas, are described here. It is shown that the rate of evaporation per unit surface of the mass frozen is always less than in vacuum, but it is possible to increase the surface considerably. The effective rates of evaporation which can be thus obtained are of the same order as in vacuum while the material involved should be far less expensive. (Author)

J. M. Dunoyer, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

36

183. Vapour Phase Conditions in Freeze-drying.

In freeze-drying processes the rate of drying is limited primarily by resistance to vapour flow from the material and through the space surrounding it, and only to a smaller extent by restrictions on the rate of heat input. Heating the material through the drying surface layers results in faster drying than when heating is effected by conduction through the frozen layer, because of an increase in the molecular motion of the vapour, which is superheated. A theory based on interphase vapour transfer is developed for this situation and for the ease of heating through the frozen layer assuming the vapour alone is heated. (Author)

J. D. Mellor, *Transactions of the Vacuum Symposium*, 1961· Pergamon Press. In press.

36 : 35

High Vacuum Drying and Impregnation Plant for Oil-filled High Voltage Cables up to 500 kV. See Abstr. No. 181.

37. Metallurgy, Inorganic Chemistry, Analytical Chemistry

37

184. A Gas-cooled Vacuum Arc Skull Furnace.

Water-cooling in titanium metallurgical furnaces has led to a number of serious explosions. The desire to overcome explosion hazards and to supply a direct method for recovery of scrap titanium, has led to the development of a 500 lb titanium scrap recovery furnace in which no water-cooling is used anywhere within the furnace shell. Heat is supplied by consumable or non-consumable d.c. arcs and electrode position is maintained automatically. The crucible is of the skull type and heat is removed by a high-pressure helium cooling system. Feeding devices permit the addition of alloys or additional scrap during operation of the furnace, and sampling from the melt is possible. (Authors)

N. Beecher and J. L. Ham, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 28

185. Melt Stock Cathode for Low Voltage Vacuum Melting Furnace. *United States.*

Vacuum melting of refractory metals is known to improve their physical characteristics. Arc, induction heating and high voltage electron bombardment methods are presently used to perform this task, each with associated problems. Another method is described offering improved melting characteristics, control of superheating, freedom from high voltage arcs and space charge problems. The method utilizes the melt stock as a source of large quantities of electrons offering unique control opportunities. Size, shape and depth of the molten pool are easily adjusted. This large electron source offers opportunity for simple, large size scale-up for higher temperature materials or larger melts. (Authors)

J. W. Griffith, W. A. Prothero and J. C. Mutton, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37

186. A Skull Furnace and its Operation. *Japan.*

Development in design and operation of a skull furnace for casting uranium or uranium alloy fuel rod is described. A newly designed bottom pouring crucible incorporated with a centrifugal casting device was used for uranium casting though tilt pouring seemed preferable for many other uses. Light pieces of $\frac{1}{2}$ in. o.d. by 6 in. long rods were cast in a vacuum less than 1 m Torr using 0–3 per cent/Zr and 1 per cent/Nb consumable electrodes. There was no contamination and segregation in the cast shape though density was slightly less than theoretical value which may be improved by heating up the mold. (Authors)

C. Hayashi, S. Kashu and T. Tsuchiya, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 28 : 41

187. Studies on Vacuum Induction-melting of Iron and Nickel. *Japan.*

The differences between iron and nickel melts concerning the dissolution or liberation of oxygen into or out of the melts in high or medium vacuum and concerning the deoxidation of the melts by carbon or hydrogen in vacuum are studied to prepare tolerably pure iron and nickel or their alloys. The remarkable differences are observed in the inclination of oxygen dissolution due to the oxygen partial pressure in medium vacuum, in the product of micro-carbon and micro-oxygen amounts in the

melts under high vacuum of 10^{-5} Torr, in the deoxidation rate by flowing hydrogen, and in the releasing rate of hydrogen out of the melts. (Author)

K. Muramatsu, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 28

188. The Megawatt Class Electron Beam Melting and Casting Furnace.

The first megawatt class electron beam furnace is described. Interesting new phenomena and different operating characteristics have been observed as this significant scale-up of electron beam melting and casting facilities has been accomplished. These differences, attributable to the size factors, are discussed here. Considerably more data has been obtained on the relation between the impurity content of metal and the melting rate and pumping speed. Productive capacity is correlated with these data ; and with the economics of electron beam melting operations as a function of raw melt stock quality. (Authors)

H. R. Smith, Jr., C. d'A. Hunt and C. W. Hanks, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 28

189. Experience with an Electron Beam Melting Furnace. *United States.*

A 60 kW remote gun, electron beam melting furnace has been used in the production of tantalum, columbium and other metals for more than a year. This experience has shown the economics of the process and has provided valuable vacuum equipment design data. Specific metallurgical data are presented including chemical analyses, melting rates, yields and physical properties of various metals. (Authors)

M. L. Torti and C. B. Sibley, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 40

190. Determination of Composition and Pressure of Gases Over the Melt in a Vacuum Arc Furnace. *United States.*

Two devices for routinely recording the composition and pressure of the gas atmosphere immediately over the melt in a vacuum arc furnace are described. One is a combination of vacuum gauges yielding percentage H_2 and total pressure. The other is a gauge connected to the shrinkage space between the ingot and the mold wall for indicating the pressure over the melt. In many experiments the latter pressure was several Torr, but very low pressures indicative of insignificant gas evolution were recorded with a " gas-free " iron. The pressure varied sensitively in an inverse manner with the arc length. The value of this information in terms of understanding and improving vacuum arc melting processes is discussed. (Authors)

E. W. Johnson, R. Itoh, R. L. Readal and M. L. Hill, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 40

191. High Capacity Vacuum Fusion Apparatus for Gas Determination in Chromium. *Australia.*

The design of high capacity vacuum fusion apparatus for gas determinations in chromium is discussed. Gettering is avoided by a maximum of 40 per cent chromium in the bath, a graphite closure to the crucible, and a high speed (80 μl/sec) mercury diffusion pump. By using a large (60 g) iron bath, and constructing the apparatus as two separate units—for gas extraction and collection, and for gas analysis—two operators can analyse sixteen samples totalling 40 g. in $8\frac{1}{2}$ hr. Recovery of oxygen is quantitative and of nitrogen 95.7 per cent (standard deviation 1.9 per cent). (Authors)

A. Lench and G. S. Martin, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 40

192. A New Vacuum Fusion Analyser for High Purity Metals.

Theoretical view on the removal of hydrogen, nitrogen and oxygen from reactive metals through vacuum treatment. Influence of temperature and carbon on the degassing process. The vacuum fusion method, principle and procedure. Problems of determining very small gas quantities in clean reactive metals. Description of a new vacuum fusion apparatus. Application of a gas chromatograph and a β-ray ionization detector for gas analysis. Practical examples of analysis. Details on pressure, degassing time and quantity of possible analyses. Analysis of very small gas amounts. Limits of method. (Author)

R. Lesser, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 28

193. Electron Beam Melting with Multiple Guns.

Principle of electron beam melting under high vacuum. Outline of ring beam system and electron gun system. Description of electron beam melting furnace with multiple separately evacuated guns. Advantages of guns over ring beam system. Different methods of melting with electron guns (addition melts, drip melts, etc.). Vacuum problems of electron beam melting. Remarks on dimensioning of pumping system to achieve high vacuum. General thoughts on degassing of reactive metals under high vacuum. Data on the purification of niobium and tantalum through electron beam melting. Application of electron beam melting for production and laboratory work. (Authors)

R. Lesser, H. Gruber, H. Stephan and W. Dietrich, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 28

194. Production Experience with a 5000 lb Vacuum Induction Furnace.

Short review of the vacuum induction melting process during the past decade. Description of a 5000 lb vacuum induction furnace (world's largest unit) with special emphasis on its novel technical features. Operational procedures in the melting process. Discussion of ingot casting methods based on recent heat flow and metal solidification investigations. Reivew of latest large scale property evaluations on wrought high temperature alloy parts. Outlook towards larger vacuum castings (10,000 lb) and future projection of new alloys and processes. (Author)

W. A. Matejka, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 16 : 30

195. The Application of Liquid Metal Circulating Systems in Vacuum Technology. *Hungary.*

A method has been recently introduced to achieve and maintain clean liquid metal surfaces by the permanent renewing action of electromagnetically forced circulation. It may be usefully applied on vacuum technology for processes governed by surface phenomena of liquid metals, the main applications being continuous metal evaporation and sorption of gases. Design principles of systems and components including electromagnetic pumps to be operated in vacuum and corrosion relations are discussed. Design and characteristics of a realized system are given. (Author)

E. I. Fazekas, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 41 : 45

196. Brazing of Sandwich Structures of Columbium Alloys.

The refractory metals are just emerging as important practical materials for high temperature applications. Almost without exception, however, practically every order involves a heavy

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measure of development as well as straightforward production. Above, say, 2500°F there are no proper criteria for design specifications. There are not even adequate testing procedures and facilities for developing such criteria. And as often as not a new operational requirement will necessitate a whole new look at materials, fabrication techniques and equipment. Designed for sintering, brazing, heat treating and annealing, a new resistance type vacuum furnace operates at temperatures up to 4500°F with pressures in the 0.1 μ range. Therefore, the investigation has resulted in the development of a ductile brazing alloy for use in vacuum which possessed superior wettability and produced ductile joints with columbium and its alloys without any interaction between braze alloy and base metal. This paper relates the development of such alloys, equipment necessary to produce the elevated temperatures and atmosphere necessary for brazing, tooling material for this new temperature range and presents some property data obtained on joints brazed with the best of these alloys and initial non-destructive techniques for inspection and the quality assurance of the brazed joints. (Author)

M. M. Schwartz, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 20

197. Vacuum Crystal Pulling Installations and Combox Systems for Manufacture of Transistors and Microelectric Components. The relation between vacuum technique and the problems involved with the production of very reliable semiconductor devices will be discussed. As example the design of a single crystal pulling apparatus using high vacuum, and experimental as well as production experience are presented. Some new components for production and laboratory application are introduced which offer many possibilities for the definition of working conditions. The results of a design study for flexible units, useful for combination of vacuum and controlled atmosphere in manufacturing processes are demonstrated. (Authors)

O. Korn and J. Moll, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37 : 42 : 53 : 28

198. Vacuum Hot Pressing of Refractory Materials. An induction heated vacuum hot press of simple design has been constructed and used for the past 2 years at this laboratory. It has proved to be an extremely versatile tool for consolidating a wide variety of refractory materials for research investigations. The equipment capabilities are : temperatures in excess of 2500°K at vacuum of the order of 10^{-6} Torr and compacting pressures of 200–300 kg/cm^2 applied to powders contained in a graphite die. (Author)

E. W. Hoyt, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

37

199. Inert Atmosphere Processing Facility for Refractory Metals. *Engineer*, **210**, 5458, p. 410, 2 September, 1960.

37 : 28 : 45

Fusion Welding of Beryllium in a Vacuum Atmosphere. See Abstr. No. 110.

37 : 22 : 27 : 40 : 51

Residual Gases in Metal Vacuum System. See Abstr. No. 85.

37 : 28 : 30 : 49

Contribution to the Problem of Electron Beam Design for Melting, Welding, Evaporation and Drilling Processes. See Abstr. No. 111.

37 : 33 : 40

Residual Gases in Closed High Vacuum Systems, Determined by Mass Spectrometry. See Abstr. No. 171.

37 : 40 : 22 : 27

Residual Gases During Operation and Life-testing of Power Klystrons. See Abstr. No. 203.

37 : 40 : 27 : 22

Analysis of Gases in an Oil Pumped Vacuum System by Use of an Automatically Controlled Mass Spectrometer. See Abstr. No. 204.

37 : 22 : 27 : 40 : 51

Mass-spectrometer Investigations in Ultra-high Vacuum Systems. See Abstr. No. 86.

37 : 21

Pump for Circulating Gases. See Abstr. No. 76.

37 : 24

Device for Admitting Gas at Constant Rate to Vacuum Apparatus. See Abstr. No. 99.

37 : 28

Controlled Atmosphere Levitation System. See Abstr. No. 112.

37 : 30

Infra-red Absorptiometer, Using Interference Filters, for Analysis of Hydrogen Fluoride in Gaseous Mixtures. See Abstr. No. 158.

38. Distillation, Organic Chemistry, Isotopic Gas Analysis

38

200. Refining of Rice Oil by Molecular Distillation. *Japan.* The production of rice oil in Japan in 1960 amounted to 39,000 tons, of which about 60 per cent are crude oils with high acid value. The remainder are crude oils of low acid value used for the production of food oil through the conventional refining process. This food oil, though very similar to cottonseed oil in its constituent fatty acids, has not yet emerged from its substitutional status. A method of molecular distillation is proposed to obtain high quality oil. The technique involves distillation after esterification of a part of the fatty acids. (Author)

K. Sakurai, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

39. Miscellaneous Applications

39

201. The Application of Vacuum to Steam Sterilizers. *United Kingdom.* The speed and certainty of steam sterilization of textiles is very greatly increased if a preliminary vacuum of 20 Torr or less is drawn in the autoclave. Recommendations for the design and operation of a so-called " high-speed " autoclave are made. The effect of varying degrees of preliminary vacuum in sterilizers loaded with textiles in different forms of pack has been investigated. A pressure below 15 Torr was indicated even when textiles were wrapped in fabric and not otherwise contained. Methods of obtaining the vacuum have also been investigated from the points of view of reliability and convenience. In general, an air-ballasted oil-sealed rotary pump protected by a condenser has been found to be a most suitable combination. (Authors)

T. W. G. Rowe, R. Kusay and E. Skelton, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

39

202. Method for Measuring the Moisture Content of Air.

United Kingdom.

The water vapour in a sample of air is first condensed as ice and subsequently allowed to evaporate at room temperature, so causing a pressure rise in a closed, evacuated system, the pressure being measured by a simple oil manometer. The apparatus for doing this is described in detail and, by a calibration of the instrument with known masses of water vapour, a factor can be obtained that converts the observed vapour pressure to absolute humidity with an overall accuracy better than 1 per cent. The apparatus has also been used to study the relationship between water vapour pressure e (mm of mercury) and absolute humidity h_v (g/m^3). A value of 286.4 ± 1.7 was obtained for the constant C in the equation $h_v = Ce/T$ where T was the absolute temperature (°K). (Author)

J. Higgins, *J. Sci. Instrum*, **36**, July 1959, 300–302.

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40. Gases and Vapours

40 : 22 : 27 : 37

203. Residual Gases During Operation and Life-testing of Power Klystrons. *United States.*

The gases present during exhaust processing, operation, and life testing of high-power klystrons were analysed using a Diatron mass spectrometer. During bakeout at 500°C, hydrogen, water, carbon dioxide and methane were evolved. Carbon dioxide, methane and carbon monoxide predominated during cathode conversion. Electron bombardment of internal tube parts released carbon monoxide. After seal-off, the pressure was 10^{-7} Torr (carbon monoxide, methane, hydrogen). 100 hr of klystron operation reduced the pressure to 10^{-9} Torr (carbon monoxide, hydrogen). Microleaks in a sealed klystron resulted in the appearance of argon ; neither oxygen nor a mass 28 increase were detected. The argon disappeared during klystron operation. (Authors)

L. Noble and R. K. Waits, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

40 : 27 : 37 : 22

204. Analysis of Gases in an Oil Pumped Vacuum System by Use of an Automatically Controlled Mass Spectrometer. *United States.*

An omegatron type mass spectrometer has been used to analyse the residual gases in an oil pumped vacuum system. An automatic controller, permitting continuous unattended operation of the omegatron, combined with a method of obtaining filament emission control for the omegatron, is described. An analysis of the gases liberated during baking of the vacuum system and evaporation of the melt, together with the effectiveness of methods of reducing these gases, is presented. (Authors)

G. R. Giedd and G. C. Roberts, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

40 : 16 : 14

The Measurement of Accommodation Coefficients of Gases on Tungsten. See Abstr. No. 33.

40 : 21 : 25

Low Temperature Cooling Experiments with Ultra-high Vacuum Pumping Units. See Abstr. No. 53.

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Determination of Composition and Pressure of Gases over the Melt in a Vacuum Arc Furnace. See Abstr. No. 190.

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High Capacity Vacuum Fusion Apparatus for Gas Determination in Chromium. See Abstr. No. 191.

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A New Vacuum Fusion Analyser for High Purity Metals. See Abstr. No. 192.

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A Portable High Speed Ultra-high Vacuum System. See Abstr. No. 45.

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Residual Gases in Metal Vacuum System. See Abstr. No. 88.

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Mass-spectrometer Investigations in Ultra-high Vacuum Systems. See Abstr. No. 86.

40 : 33 : 37

Residual Gases in Closed High Vacuum Systems, Determined by Mass Spectrometry. See Abstr. No. 171.

41. Metals and Alloys

41 : 37 : 28

Studies on Vacuum Induction-melting of Iron and Nickel. See Abstr. No. 187.

41 : 37 : 45

Brazing of Sandwich Structures of Columbium Alloys. See Abstr. No. 196.

41 : 33

Surface Structure of Saturated-diode Filaments. See Abstr. No. 172.

42. Glass, Ceramics and Refractory Oxides

41 : 21 : 27

205. The Use of Semiconductors in High Vacuum. *Jugoslavia.*

In recent years it has been found that the excellent thermoelectric parameters, as well as the small size and heat capacity of semiconducting oxides, make them a valuable element in high vacuum technology. In this paper a survey of investigations made until now in the use of semiconductors for the construction of manometers, leak detectors and various vacuum accessories is given. For a better understanding of this problem a brief description of the basic properties of semiconductors is included. Further, an oscillographic method to investigate the possibility of extending the working range of thermistor gauges to low pressures is discussed. (Author)

M. Varićak, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

206. Direct Deposition of Sulfide Glass Films by Evaporation. Flaschen, Pearson, and Northover have previously reported on " Low-melting inorganic glasses with high melt fluidities below 400°C ". These glasses* are being used for the protection of solid-state devices against the harmful effects of atmospheric moisture ; they consist of binary or ternary mixtures of thallium, arsenic, and sulfur which are fluid in the range of 200–400°C ; they are available in powder form or as preforms pressed from powder but can also be produced by vacuum deposition as thin film on the order of 1 mil thick. For dip coating, the powder is molten in specially prepared fused-silica containers to preserve their purity, and the device to be coated is immersed in the molten glass for 10–20 sec and then withdrawn and allowed to cool to room temperature. The operation is carried out in an inert atmosphere, such as nitrogen, under a fume hood to remove any toxic vapors evolved during heating. Satisfactory electric performance of coated semiconductor devices has been demonstrated in exposure to 100 per cent relative humidity for several months. In the present note, the writers describe results of a controlled study of the vaporization of these sulfide and selenide systems in vacuum employing a standard vapor coating unit such as is used in metallizing plastics. Microscope glass slides, fused silica, Teflon, aluminum, gold, and molybdenum were successfully coated in this manner. The preparation of thin films (<20,000 Å) requires no special care, but for thick films (>75,000Å) time of evaporation and target temperature must be carefully controlled. " Some fractionation in the vapor phase usually occurs which leads to a concentration gradient in the film that is dependent on the amount of self-diffusion which the system has undergone. No effects arising from this gradient have been shown as yet ".

It has been established by electron diffraction measurements that the films are indeed of a glassy nature rather than crystalline or amorphous and that they show no tendency to recrystallize even near the softening point.

" The measurements of film properties have been centered on glass films of the system As—S—Tl with prime emphasis on the high-resistivity films on the As—S binary. The remarks that follow refer specifically to this ternary system.

" Chemically, the films are inert to most common reagents except bases and oxidizing agents, such as bromine and concentrated nitric acid.

" Physically, the films are soft with a value of about 4 on the Mohs hardness scale and are easily abraded. Optically, the films along the As—S binary are red at As_2S_3 and become more yellow as the sulfur content is increased. The index of refraction (5461 Å light) ranges from 2.11 for a 15 per cent As, 85 per cent S glass to 2.77 for As_2S_3. The thallium-containing glasses are a wine red which deepens with increasing thallium content.

" Electrically, the films along the As—S binary have high resistivity (10^{12} to 10^{16} ohm.cm), exhibit low loss (Q's >650 have been measured), and have high dielectric breakdown strength ($>10^6$ V/cm). All these properties are somewhat difficult to measure on thin films and there is scatter in the measurements. The quoted values are believed to be realistically conservative. The films are continuous as is indicated by electron micrographs which show a continuous structureless pattern. Further indications of complete continuity are supplied by the high resistivities obtained on thin (1000 Å) films using evaporated metal electrodes and by the high dielectric breakdown values obtained with a similar electrode system ". W.H.K.

*Available from Baker and Adamson, 40 Rector Street, New York 6, N.Y.

W. R. Sinclair, S. S. Flaschen, and F. G. Peters, *J. Amer. Ceram. Soc.* **43**, 168, March 1960.

42 : 17

High Temperature Reactions of Silica-glass with several Metals in a Vacuum. See Abstr. No. 37.

42 : 37 : 53 : 28

Vacuum Hot Pressing of Refractory Materials. See Abstr. No. 198.

43. Plastics and Elastomers

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High Vacuum with the Polyphenyl Ethers—a Self-contained Technology. See Abstr. No. 207.

44. Waxes, Lubricants, Cements, Lacquers, Paints, Oils

44 : 43 : 54

207. High Vacuum with the Polyphenol Ethers—a Self-contained Technology.

The polyphenyl ethers, consisting of chains of benzene radicals interbonded by oxygen are useful in high vacuum because of their exceptional stability. The isomer mixture, *bis*(phenoxyphenoxy) phenyl ether, has a vapor pressure at 25°C of $\sim 10^{-9}$ Torr and yields vacuums approaching 10^{-9} Torr in the unrefrigerated condensation pump. Applied to gaskets, valves and joints or as a coating to large inside metal surfaces they enable ultra high vacuums to be induced rapidly and economically on any desired scale of operation. Five examples, with quantitative data are described, ranging from the single stage glass pump to an oil-sealed container evacuated by fractionating metal pumps. (Author)

K. C. D. Hickman, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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Materials Evaluation Under High Vacuum and Other Satellite Environmental Conditions. See Abstr. No. 177.

45. Soldering, Welding, Brazing, Solders

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Fusion Welding of Beryllium in a Vacuum Atmosphere. See Abstr. No. 110.

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Electron Beam Welding of High Strength Alloys. See Abstr. No. 166.

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High-power-density Electron Beam Welding of Several Materials. See Abstr. No. 167.

45 : 33 : 28

Electron Beam Processes at Different Voltages. See Abstr. No. 168.

45 : 33 : 28

Studies on Electron-beam Welding. See Abstr. No. 169.

45 : 37 : 41

Brazing of Sandwich Structures of Columbium Alloys. See Abstr. No. 196.

47. Outgassing Data, Vapour Pressure Data, Gettering Data

47 : 31

208. Properties of Modern Barium Getters. *United States.*

New barium getters are discussed. The flashing temperature can be reduced by adding metals to the getter alloy that react with this alloy exothermically. Details of the chemistry of the exothermic reaction are given. The influence of quantity and distribution of the evaporated barium on the functioning of the getter are discussed. This is done by measuring both barium distribution and gas adsorption in structures having the same geometry as actual receiving and television picture tubes. In the latter case, the data obtained will allow conclusions concerning the influence of barium quantity and distribution on picture tube life. (Authors)

R. Cols, C. W. Reash and J. S. Wagener, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

47 : 16

209. The Origins and Composition of the Limiting Gas Load in Ultra-high Vacuum Systems. *United States.*

As a step forward achieving lower pressures as well as a step toward better understanding of ultra-high vacuum technique, a basic study was made of the origins and nature of the residual gases present when operating in the 10^{-9}–10^{-10} Torr range. The relative importance of real air leaks, sealant permeation, surface outgassing, vapor backstreaming, and back diffusion of gas was investigated. The role of each of these factors is discussed and recent research results cited. The meaning of these findings to the design of ultra-high vacuum systems is pointed out. (Authors)

I. Farkass and E. J. Barry, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

47

210. Degasification of Different Metallic High Vacuum Materials.

Several metal samples with various types of surface treatment were heated according to a previously determined temperature cycle. The liberated gases were then measured with partial-pressure meters like " farvitron " or " omegatron ". Differences were observed as to the nature and quantity of the liberated gases. These differences were due to the various methods of de-greasing, the applied method of plating and also to the nature of the various raw materials. (Authors)

F. A. Flecken and H. G. Nöller, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

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211. Outgassing. *Germany.*
The paper begins with a compilation of data on gas-formation velocities obtained by various authors as well as by ourselves. It is found that gas-formation velocities depend on the material, its treatment and the conditions of its particular application. A knowledge of the principal physical processes (like physical and chemical sorption, diffusion, solubilities, etc.) which mainly determine the process of gas formation is necessary in order to establish the most favourable conditions for the evacuation of high-vacuum apparatuses. The lowest pressures attainable at present in high vacuum systems can then be deduced by taking the data on gas formation mentioned above in conjunction with the corresponding physical laws. (Author)

R. Jaeckel, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

47

212. Outgassing Data for Several Epoxy Resins and Rubbers for the Zero Gradient Synchrotron.
This paper presents outgassing measurements made on several types of epoxy resins and on several rubbers. Measurements on steel and aluminum are given for comparison. These are all long term measurements of the outgassing over a period of from 0.1 to 500 hr under vacuum. The data were taken by measuring the rate of pressure rise in a closed volume, and the advantages and limitations of the system will be discussed. Many detailed data on the outgassing of the nitrile-phenolic adhesive used for bonding and sealing the high vacuum chamber of the ZGS machine will be presented. (Authors)

F. Markley, R. Roman and R. Vosecek, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

47 : 21

213. Pumps as a Gas Source. *United States.*
In dealing with vacuum systems the problem of the pump being a gas source is often encountered. A discussion of mechanical, diffusion, getter, getter-ion pumps and traps will show how they can limit the ultimate pressure and what can be done to eliminate these problems. A method of analysis to determine how this phenomenon takes place will be included. (Author)

F. Pagano, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

47

214. Gas Absorption Properties of Barium Getters for Use with TV Picture Tubes. *Japan.*
The sorption velocities of various pure gases by a variety of barium getters flashed in a 14-in. picture tube which had undergone an ordinary manufacturing process were measured while maintaining a constant gas pressure on the evaporated barium film. The influence of different gases on the activity of oxide cathode was also examined during the measurement. Some results obtained are : sticking probability's being independent of the surrounding gas pressure after a monatomic layer equivalent absorbed ; variously changing sorption characteristics among various types of getters, between getters of different film areas and with changes in the amount of barium flashed ; and much improvement in both final vacuum and electron emission by the scanning of a tube. (Authors)

H. Takayama and H. Kobayashi, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

47

215. Effect of Pretreatment on the Degassing of Materials. *United States.*
The time required to reach the ultimate pressure in a vacuum system depends on the speed of degassing of its components. It was observed that gas quantity and the speed of gas evolution can be changed by various pretreatments. A fast dynamic measuring technique—described previously—was utilized to study the effect of the different pretreatments (e.g. chemical cleaning, hydrogen firing, storing, handling) on the total gas quantity evolved, on its composition, and on the speed of gas evolution from nickel. (Author)

P. F. Varadi, *Transactions of the Vacuum Symposium*, 1961. Pergamon Press. In press.

47 : 16

Outgassing Rate of Contaminated Metal Surfaces. See Abstr. No. 21.

47 : 16

The Desorption of Ionically Trapped Argon from Tungsten. See Abstr. No. 28.

47 : 11

Investigations Concerning Bulk Getters from Metals of the IVth A Group and Thorium. See Abstr. No. 4.

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A Low Pressure Evaporation Plant for Rapid Operation. See Abstr. No. 147.

48. Heating, Refrigeration, Ultrasonics, Centrifuging

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Materials Evaluation Under High Vacuum and Other Satellite Environmental Conditions. See Abstr. No. 177.

48 : 28

A Method of Producing Eddy-current Heating. See Abstr. No. 113.

49. Miscellaneous Materials and Techniques

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216. Sublimation of Cr_2O_3 at High Temperatures.
The sublimation of chromic oxide, Cr_2O_3, has been observed in vacuum by the Langmuir technique using induction and solar heating. Extensive sublimation did not yield any new phases on the basis of X-ray powder studies, and condensates of Cr_2O_3 were always obtained. Flash vaporization and flow experiments in CO or O_2 atmospheres and in vacuum indicated no appreciable differences in rates of sublimation. Weight-loss experiments showed that the rate of sublimation was slightly higher than predicted for decomposition to the elements and suggested that small amounts of complex molecules, e.g. CrO and CrO_2, were also present in the equilibrium vapor. (Authors)

K. Wang, L. Dreger, V. Dadape and J. Margrave, *J. Amer. Ceram. Soc.*, **43**, 509–510, October 1960.

49

217. Photoelectric Double-slit Interferometer for Investigation of Transparent Thin Solid Films.
United Kingdom. The interferometer is of the Rayleigh two-slit type. The film to be measured is deposited on part of a glass plate which is then placed in front of the slits so that both are covered by the plate but only one by the film. The phase retardation due to the film is then measured by a compensating plate. To improve location of the fringe minimum, an extra plate of glass is made to oscillate at 10 c/s and the light is detected by a photomultiplier and synchronous rectifier. A sensitivity of $\lambda/7000$ is claimed. The equipment has been used to investigate the instability of evaporated films of ZnS.
(Author, modified)

Lee Sang Soo, *J. Sci. Instrum.*, **36**, 385–387, September 1959.

49

218. Dielectric Measurements on Thin Films by Means of Electrodes Coated with Irradiated Silicone Rubber.

United Kingdom. The difficulties in measuring the dielectric properties of thin films by conventional methods are discussed and an alternative method of measurement is described. The new method uses electrodes faced with a rubber-like material ; the capacitance and loss tangent are measured with and without the thin film specimen pressed between the flexible surfaces. The constants of the specimen can then be calculated. Irradiated polydimethylsiloxane was the only material found to be suitable for the electrode facings at high frequencies and high temperatures. (Author, modified)

W. P. Baker and F. B. Waddington, *J. Sci. Instrum.*, **36**, July 1959, 309–312.

49 : 28 : 37 : 30

Contribution to the Problem of Electron Beam Design for Melting, Welding, Evaporation and Drilling Processes. See Abstr. No. 111.

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Quick Method of Computing the Transmission of Zinc Sulphide-magnesium Fluoride Multilayer Filters. See Abstr. No. 159.

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51. Physics, Astronomy, Geophysics

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220. On the Present State of the Units Problem in Vacuum Science and Technology. *Belgium.*

Although it has again been suggested recently to replace pressure by another quantity for characterizing the degree of gas rarefaction, the necessity of an agreement on the unit of pressure keeps all its interest. We examine the solutions adopted or proposed during these last years. These solutions pertain to two groups according to the recommendation to use : (a) the unit of pressure of the International System of Units or any decimal submultiple of it ; (b) units of pressure not pertaining to this system such as millimeter of mercury, Torr, etc.

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V A C U U M

Papers to be published in future issues

G. von Vick : Friction Effects in a Satellite Environment—The Present State of the Art.

B. Cobic, G. Carter and J. H. Leck : Further Investigations of the Bistable Operation of the Bayard–Alpert Gauge.

E. E. Brueschke : A Leak-free Method of Transmitting Motion into Ultra-high Vacuum.

R. J. Hill : The Adsorption of Water on Tungsten.

J. S. Collingon : Ion Bombardment of Metal Surfaces.

S. H. Shortes and D. P. Miller : Observations of Crystal Orientation Effects in Tin-Telluride Thin Films.

Editorial

ARRANGEMENTS are now well advanced to bring the scheduled publication date of *Vacuum* into step with the actual date issued. Towards this end the present issue combines Numbers 5 and 6, and concludes Volume 11 for 1961.

Readers will notice that in Numbers 4 and 5/6, the Abstracting Section includes hitherto unpublished abstracts of all papers published in Volumes 9 and 10 of *Vacuum*, together with abstracts of all papers contributed to the important Eighth Vacuum Symposium of the American Vacuum Society held in Washington in 1961 in conjunction with the Second Congress of the International Organization for Vacuum Science and Technology. Abstracts of Volume 11 will appear in an early number of Volume 12, and thereafter abstracts of the journal will be printed currently. Attention is drawn to the preliminary report of the Abstracting Editor on page 291 in view of the great importance attached to this part of the journal.

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The Editorial Board will welcome comments and suggestions from readers to help in their work of maintaining *Vacuum* as the international journal and abstracting service for Vacuum Science and Technology.

A. S. D. BARRETT

VACUUM

Further Investigations of the Bistable Operation of the Bayard–Alpert Gauge

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Observations of the influence of the electron emission current, the electron collector potential, gas composition and wall cleanliness upon the bistable operation of the Bayard–Alpert gauge are reported. This bistable behaviour is observed as a duality of manometric sensitivities and ion pumping speeds and the magnitude and variation of these with electron collector potential was measured in both modes of operation for several gases. It is concluded that it is advisable to operate gauges at electron collector potentials less than 250 V, to avoid instability and maintain optimum sensitivity.

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Introduction

Since its introduction in 1950 the Bayard–Alpert[1] gauge has been widely used for the measurement of low pressures (10^{-3}–10^{-11} Torr). Alpert[2] and others[3] have discussed its merits and disadvantages and recent publications[4, 5] have indicated methods of overcoming some of these latter. One of the disadvantages of the gauge, which has been the subject of investigation in this[6] and other laboratories[7], is the fact that the glass walls are exposed to electronic and ionic bombardment which gives rise to instability in the operation of the gauge. Since glass is an insulator, the charged particle bombardment of its surface leads to the acquisition of some potential by the surface, which in the equilibrium condition is such that there is no net rate of charge gain or loss.[8] Earlier work[5, 6, 7] has shown that the surface potential, in certain circumstances, can attain either of two values, one close to cathode potential, at which the primary electron bombardment is balanced by the ionic bombardment, or a second, close to anode potential, at which the primary electron current is balanced by a secondary electron current emitted from the walls by the bombarding electrons. It has been shown[6] that, according to the prevailing wall potential the gauge possesses one of two possible manometric sensitivities and simultaneously one of two ion pumping speeds. In the present work this phenomenon was observed under a wide range of conditions in which the parameters gas constitution, gas pressure, electron emission current and electron energy were varied and their effect upon the mode of operation studied. In addition values for the sensitivity of the gauge for the inert gases and the variation of this with electron accelerating voltage, of some technical importance, were obtained.

Experimental

Two methods, both described in detail elsewhere,[6] were used to observe the dual mode of operation of the gauges. In the first apparatus, used for much of the earlier work and employing a dynamic technique, gas at a known rate was continuously passed through the experimental gauge for a known time and under specified operating conditions and the pumping action of the gauge was observed by subsequently recording the gas recovered from the gauge on heating. The sensitivity of the gauge to different gases was measured simply by knowing the flow rate through the system and the effective pumping speed at the system. The second method, used for the present work and employing a static technique, relied on measurements of the pumping speed of a gauge by observing the time rate of fall of gas pressure in the isolated system. The variation of gauge sensitivity with various parameters was observed by comparison with another gauge in the isolated system operated under standardized conditions. In both methods the apparatus could be baked to about 400 °C thus enabling the attainment of pressures lower than 10^{-9} Torr and ensuring a reasonably reproducible experimental glass surface. The wall potentials were estimated using a capacitance probe cylinder method or by observation of the operating gauge sensitivity. The gauge envelope was about 5 cm i.d. × 15 cm long. The electron collector was a nickel helix of 2 cm dia., 8 cm length and 1 cm pitch. The nickel ion collector was located axially in the bulb (and electron collector) and the two filaments were located midway between the electron collector and the envelope.

Results

The earlier work showed that, if the electron collector potential was about 250 V, the walls could stabilize at either anode or cathode potential, depending, apparently, upon the cleanliness of the walls. Measurements with a gauge in which a metal cylinder close to the inner wall was included[9] tended to confirm this. It was realized that the gas pressure, electron emission current and chiefly the electron accelerating potential could influence the mode of operation and so the investigations described here were undertaken. It was also established earlier that the order of application of the

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gauge potentials was important in determining the mode of operation of the gauge and this phenomenon was used in the present measurements as a probe to determine the operating mode of the gauge. To do this the gauge filament was activated at a temperature corresponding to the lowest practicable emission, and the gauge walls would stabilize at approximately cathode potential. The operating conditions of H.T. voltage and emission current were then established and the mode of operation of the gauge observed via its sensitivity and pumping speed. This technique enabled wall prestabilization at cathode potential and the effects of gradual changes in operating parameters could be observed subsequently. Alternatively the operating conditions could be established immediately upon or before activating the filament and the resulting wall stabilization observed.

It was found that at all pressures (10^{-9}–10^{-4} Torr) all emission currents ($\frac{1}{4}$–5 mA) and electron accelerator potentials below 250 V in the gauge employed, the walls invariably stabilized at cathode potential whatever the order of application of filament activation and electrode potentials. In earlier experiments, when the glass was relatively poorly outgassed, wall anode potential stabilization was observed at 250 V. This case was never observed in the present measurements however, when it is of some significance, the walls had undergone stringent baking. If, however, the electron collector potential was slowly increased above 250 V, while the emission current was maintained at a low value ($\frac{1}{4}$ mA) at some potential the wall potential became unstable and possibly increased to the anode value. The electron collector potential at which wall potential oscillation occurred was observed to decrease with increasing gas pressure, as indicated in Table I. If the wall potential was maintained

TABLE I

Electron collector potentials at which the gauge became unstable and reverted to mode "A" operation.

Pressure (Torr)	Instability potential (V)	Reversion to mode "A" potential (V)
6×10^{-9}	—	—
3×10^{-7}	380–390	—
5×10^{-7}	370	—
4×10^{-6}	345–350	490
1.6×10^{-5}	320	365
3.4×10^{-5}	320	350

at an unstable position and the electron current slowly increased from $\frac{1}{4}$ mA, at a critical value of the emission the wall potential suddenly fell to the cathode value and stabilized. It is interesting to note that in a gauge in which a metal can screened the inside walls, a similar phenomenon occurred. The metal initially stabilized at anode potential at a low emission current, but upon increasing the current the metal potential slowly dropped until a critical current was reached at which the metal reverted to cathode potential. The explanation offered for this latter behaviour was that the electron collector potential fell as the emission was raised because of control unit limitations, but in the former case no such limitation was imposed upon the tube and some other mechanism must have operated.

Another interesting observation made at higher electron collector potentials was that if the walls were stabilized at cathode potential and the gauge allowed to pump, more gas then admitted and the pressure reduced again and the process repeated several times. Then when the third pump down was commenced the walls became stabilized at anode potential, even though the pressure may be low enough to allow cathode potential stabilization in a clean gauge. The gas charge of the walls thus appeared to be a factor influencing their stabilization. At each electron collector potential, the manometric sensitivity and the ion pumping speed of the gauge were measured for both wall potentials where possible, for several gases. In Table II are given the values of the

TABLE II

Manometric sensitivity of a Bayard–Alpert gauge relative to argon under mode "B" conditions

Operating conditions:
Cathode–Electron collector potential = 260 V
Cathode–Ion collector potential = −20 V
Electron emission current = 1.0 mA

Gas	Relative sensitivity	
	Present work	After Schulz
Helium	0.17	0.14
Neon	0.26	0.22
Argon	1.0	1.0
Krypton	1.53	
Xenon	2.22	

gauge sensitivity, with the walls at cathode potential, for various gases, and in Fig. 1 the variation in sensitivity with electron accelerating voltage for these gases is shown. The sensitivity in the so called mode A of operation, walls at anode potential, was observed to be between three and four

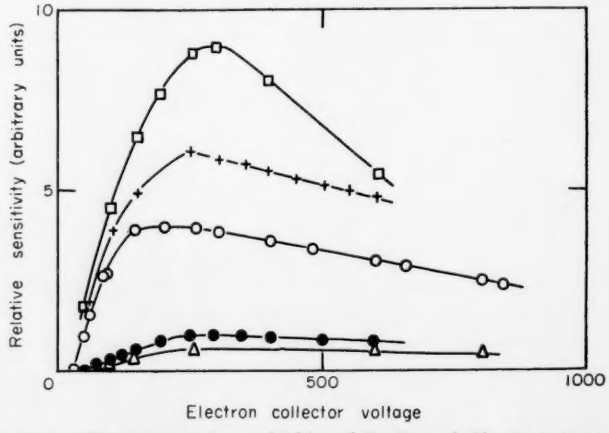

FIG. 1. The manometric sensitivities of the Bayard–Alpert gauge to the inert gases relative to argon, as a function of the electron collector voltage.

△ Represents helium
● Represents neon
○ Represents argon
\+ Represents krypton
□ Represents xenon

times smaller than under mode B operating cathode wall potential conditions for values of the electron collector potential above about 350 V; this is indicated in Fig. 2

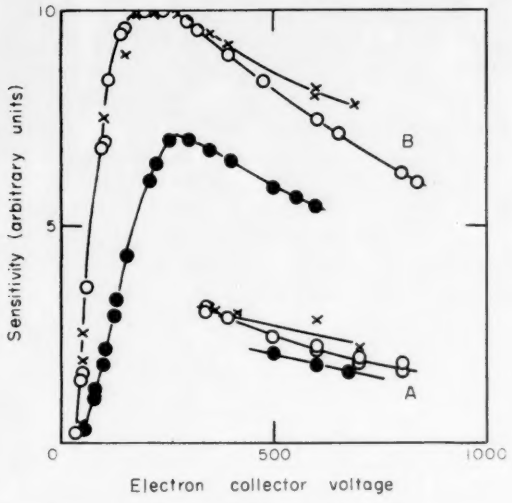

FIG. 2. The manometric sensitivities of the Bayard–Alpert gauge to argon, neon and nitrogen in both modes of operation as a function of the electron collector voltage.

× Represents nitrogen
○ Represents argon
● Represents neon

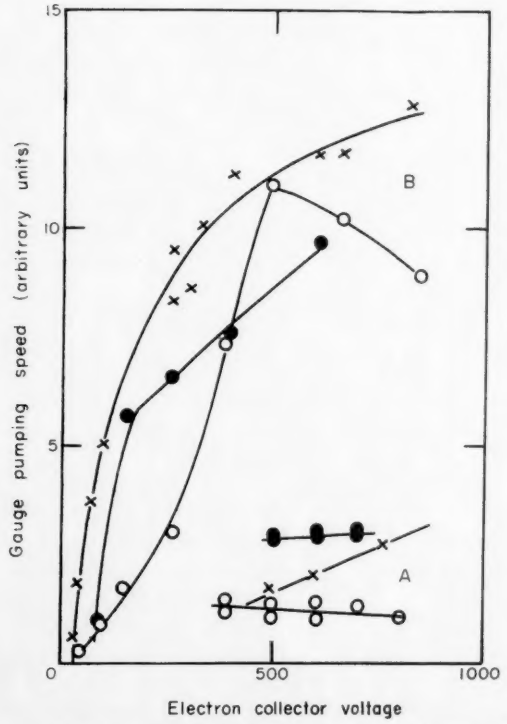

FIG. 3. The initial pumping speeds of the Bayard–Alpert gauge for argon, neon and nitrogen in both modes of operation as a function of the electron collector voltage.

× Represents nitrogen
○ Represents argon
● Represents neon

where the sensitivities of argon, neon and nitrogen in both modes are shown. Simultaneously the gauge pumping speed under mode B conditions was found to be between about three and ten times as large as under mode A conditions according to the operating voltage. This variation for argon, neon and nitrogen is shown in Fig. 3.

Since the manometric sensitivity of the gauge is indicative of the rate at which ions strike the collector, and therefore the rate at which they are formed, and the pumping speed is indicative of the rate at which ions are captured by the walls, then the inverse ratio of these quantities should be indicative of an ion capture efficiency. The value of this efficiency under both mode A and B conditions has been evaluated

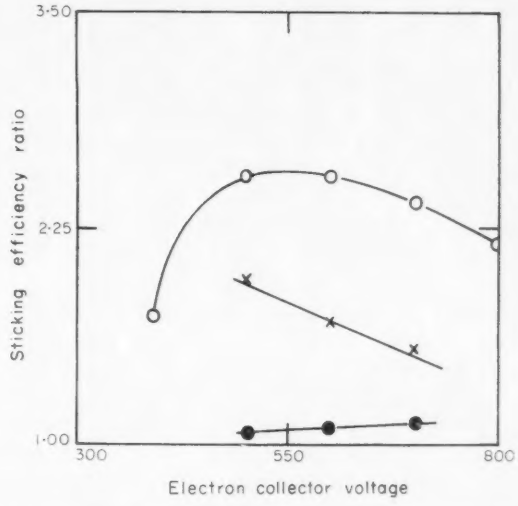

FIG. 4. The variation of the ratio of the sticking efficiencies (mode B : mode A) with electron collector voltage for argon, neon and nitrogen.

× Represents nitrogen
○ Represents argon
● Represents neon

and in Fig. 4 the ratio of the ion sorption efficiencies mode B : mode A is shown as a function of the electron accelerating voltage for the gases investigated.

Finally, since the important parameter determining the pumping speed under mode A conditions will be the value of the wall potential, observations of the value of this at different electron collector potentials, made in a tube of simple diode structure, are of interest. Measurements with a Bayard–Alpert gauge of the wall potential, were impracticable since, as has been discussed elsewhere, this latter would not be expected to be constant over the wall surface because of gauge asymmetry. The electron collector was initially held at 1500 V and the wall potential investigated with a probe can around the gauge, then upon reduction of the former the behaviour of the latter was noted. A roughly linear reduction of wall potential with grid voltage was observed, as in Fig. 5, until at a value of the latter of about 250 V the former reverted to cathode potential. This indicated a difference of potential between collector and walls varying from about +70 V to +200 V.

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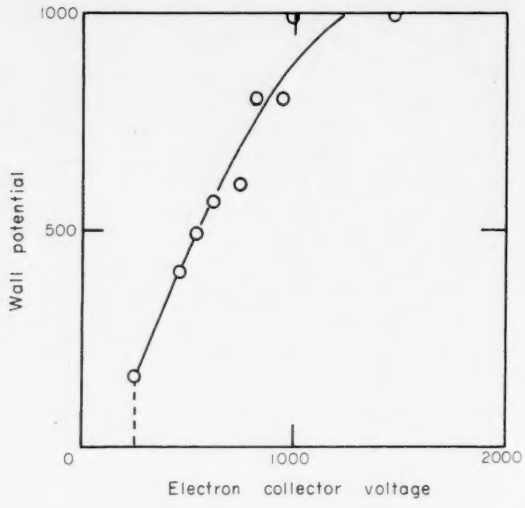

FIG. 5. The variation of the wall potential with electron collector potential in a diode geometry tube.

Discussion

In earlier work[6] it was shown how the variable wall potential could account for the observed variations in gauge sensitivity and pumping speed. The former a result of changes in ion production rate because of variable effective electron ionization path lengths and the latter the result of changes in the ion production rate and of the average ion bombardment energy. To a first approximation one can thus represent the ratio of the sticking efficiencies in the two modes by the ratio of the product (speed in mode B) times (sensitivity in mode A) to the product (speed in mode A) times (sensitivity in mode B), as shown in Fig. 4. One would expect to obtain a result in excess of unity since one anticipates higher ion sticking efficiency at the higher mean ion energy obtaining under mode B conditions. It is difficult to analyse the manner of variation of this sticking efficiency ratio with increasing electron collector potential, since at higher potentials, multiple ionization effects become important and neither is the sensitivity a reliable guide to the surface ion bombardment nor is the mean ion energy a simple function of the electron collector potential. Approximate calculations for a tube of cylindrical symmetry show that the mean ion energy increases roughly linearly with electron collector potential, under mode B conditions, while experiments indicated that the mean ion energy under mode A conditions should decrease with electron collector voltage. Since it is likely that the sticking efficiency increases with increasing ion energy, as established in earlier measurements, the ratio of efficiencies in mode B to mode A would be expected to increase with increasing electron collector potential. This is indeed observed for neon and over part of the voltage range for argon. The reverse behaviour of nitrogen and the remainder of the argon characteristic, it is believed is a result of the inadequacy of the simple diode representation to describe exactly both the ion energy and the bombardment rate. However the change in apparent sticking efficiency ratio is not very great in any case and appears to be of reasonable magnitude.

The exact cause of the dependence of operating mode upon gas pressure and emission current is somewhat obscure but the preferential tendency to stabilization of the wall at anode potential at high values of the latter is understandable. The secondary electron emission of glass remains in excess of unity for primary energies of up to about 1 kV[10], and consequently the bombardment of the glass with high energy electrons allows the possibility of high wall potential. Within limits the higher the incident electron energy the greater will be the charging rate and probability of the high wall potential. Further, the higher the electron collector potential, the higher will be the voltage induced upon the wall by initial capacitive effects and the greater will be the probability of subsequent stabilization under mode A conditions.

For equilibrium in the higher voltage mode of operation the primary and secondary currents must balance and if it is assumed reasonably that the fraction of electrons emitted by the wall and captured by the anode is an increasing function of the potential difference between the two, then since the secondary emission coefficient of glass reaches a maximum at about 300 V[10] and then decreases continuously with voltage, the voltage difference between anode and wall will be expected to become more negative with increasing anode potential. This is in fact observed in the diode tube.

The apparent mode A sticking efficiency is found to increase only slightly with increasing collector potential. This would be expected in a tube of diode structure where the wall potential never exceeds the anode potential, even at high values of the latter, but in a Bayard–Alpert type structure, because of electrode asymmetry there may be a potential distribution around the glass which leads to a roughly constant mean ion bombardment energy as the anode potential is increased.

It may be that in a tube of such asymmetry as the Bayard–Alpert gauge the region of the tube in closest proximity to the heated cathode always remains stabilized at about cathode potential, since this region of the glass may be semi-conducting at the temperature induced at its surface by the local heating and low energy electrons may reach this region more readily from the cathode. Thus sorption will be possible in the A mode with the same functional dependence of speed upon voltage (as shown in Fig. 2) but since pumping is restricted only to a fraction of the wall the magnitude will be lower. Since it is expected that the similar fractions of the wall will be affected at all values of electron collector potential, the dependence of sensitivity upon this parameter should be similar in both modes since the portion of the wall at high potential should remove the same proportion of electrons, effective in contributing towards the ion collector current. This similar variation of sensitivity with the electron collector potential in both modes is observed, as shown in Fig. 3, for the gases argon, neon and nitrogen, the characteristics of which are vastly different.

In support of the belief that the area of glass close to the cathode is the sink of the pumped gas, it is noted that when measurements of the thermal desorption of the sorbed gas after pumping in both modes are made, the release of gas

after mode A pumping does not commence until the surface temperature is about 125 °C compared to 70 °C after mode B pumping. Since it is unlikely that the incident ion energy is higher under mode A conditions, it is concluded that the sorbed gas is located in a region of higher temperature, i.e. the cathode region.

As remarked earlier, a convincing explanation of the effects resulting from pressure and emission current changes is not possible. In the metal screened gauge the inadequate emission control supply which allowed a decrease of electron collector potential (of about 20 V) with increasing emission current was almost certainly the reason for the reversion to low wall potential at high emission currents where the electron energy was insufficient to cause anode potential stabilization. This unit was not used for the unscreened gauge and the only alternative explanation which can be offered for the low mode preference is that, at high emission currents, the electron space charge prevents adequate escape of secondary electrons from the walls, causing the wall potential to fall so that a larger field is presented to escaping secondaries. The situation may become unstable and lead to cathode potential acquisition. The asymmetric structure of the gauge and the distinct possibility of a potential variation around the walls may also contribute to the instability.

The increase of gas pressure, with a resulting increase in ion density and positive space charge may have the reverse effect in encouraging the escape of secondary electrons, allowing a smaller potential between electron collector and walls, hence an increase in wall potential. It is interesting to note that at the pressures where wall instability becomes noticeable, at normal operating potential, i.e. about 10^{-4} Torr, the positive ion space charge, in argon, is of similar order of magnitude to the electron space charge. We may note that, in a gauge including a tin oxide conducting coating on the interior walls, Ehrlich[11] has observed that, at a wall potential in the cathode region, an increase in electron current results in a lowering of the wall potential, while an increase in the gas pressure results in an increase of the wall potential. Observations in agreement with the present measurements. The observation of the tendency to mode A stabilization with increasing surface gas coverage is indicative of a higher secondary yield from a contaminated surface. This phenomenon is well known when the contaminant is in the form of adsorbed gas and outgassing of surfaces generally leads to a reduction in γ. This effect in fact may be operative during observation of the pressure and emission behaviour and makes any definite explanation of these phenomena impossible.

Because of this, and the complicating difficulties of asymmetric gauge structure, it is not believed possible, nor useful, to attempt more detailed analysis of the behaviour. It is felt that a comprehensive study under more idealized conditions would be necessary to fully explain the idiosyncrasies of the gauge behaviour.

During mode B operation, however, meaningful values of the gauge speed and sensitivity can be deduced and from Table I we see the measure of agreement between present values of relative sensitivity and those of other workers[4] is as good as may be expected. The present data was recorded on a gauge the dimensions of which differed somewhat from that used by Schulz[4] and which was operated at 250 V electron collector potential. Recently Ehrlich[11] has indicated that the relative sensitivities of a commercial Bayard–Alpert gauge to N_2 and Xe are in the ratio of about 1 : 2.5. Since the sensitivity to N_2 and A are probably very close, the present estimate of the relative sensitivity of A to Xe = 1 : 2.2 is in good agreement with Ehrlich's value. The measure of agreement is therefore acceptable and the new value of relative sensitivity (for krypton) is probably reliable. The variation of gauge sensitivity with electron collector potential is of similar form to earlier data published by Dushman[12] which, however, referred to a conventional triode type gauge, and has the expected characteristic similar to the gas ionization probability function. These curves do indicate that little is gained (in the way of sensitivity) by gauge operation at greater than 250 V, while in fact deleterious effects may arise because of increased pumping action and wall instability.

Conclusions

Earlier work on the bistable behaviour of the Bayard–Alpert gauge has been substantiated and extended to include the effects of various tube parameters. Gauge asymmetry renders exact interpretation of the results impossible but the general nature of these is as anticipated. Useful information regarding the sensitivity and pumping speed of the gauges for various gases at different electron energies has been obtained and the necessity of exercising caution in interpreting pressure readings because of the wall instability pointed out.

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Friction Effects in a Satellite Environment—the Present State of the Art

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HISTORICALLY, an understanding of the existence and basic behavior of surface friction extends, as do many scientific phenomena, to the observations of Leonardo da Vinci: " Friction produces double the amount of effort if the weight be doubled ", and " the friction made by the same weight will be of equal resistance at the beginning of movement, although the contact be of different breadths and depths ". These observations were later to become identified also with Amontons who in 1699 reported much to the same effect.

Since these early attempts toward the investigation and understanding of surface friction, efforts have been continued to develop a clear understanding of the nature of frictional forces. However, this subject has not received proportionate attention in comparison to other fields and subjects. Partly because of this and partly because the subject is of a complex and enigmatic nature, the progress toward a generally accepted concept of the mechanism of friction has been extremely slow and there is no appreciable evidence that achievement of the goal is forthcoming.

Recently, Litton Industries Space Research Laboratories and the Air Force Office of Scientific Research have completed extensive research work in the field of high vacuum friction; the resulting compendium has advanced this field far beyond the concepts generally adhered to prior to the entry of these major contributors.

While existing theories of surface friction provide, in most cases, a plausible explanation of the grosser effects, no theories exist which remain consistent with the more subtle aspects of the observations which have been recorded. Furthermore, none provide any means for predicting coefficients of friction, nor is the capability provided to adjust parameters and conditions to achieve desired friction coefficients for engineering applications (except to the extent that tests for these specific conditions have been carried out and results tabulated).

One of the long-standing theories still accepted is that of Coulomb. This theory takes account of the microscopic irregularities of presumably plane surfaces. Actual areas of contact are assumed to occur at different points with random angularity. The force required to overcome friction is taken to be that required to cause a block to slide up the contact plane to a new interlocked or stable orientation of contact areas. The general nature of this concept is accepted by Brinkerman and other authorities. However, many prominent people involved in this phase of physics were not receptive to this theory for various reasons. Strong and Lewis, for example, report experimental tests showing that only a few per cent of the measured friction can be accounted for as Coulomb friction.

A point of view which appears to have originated with Ewing, and more recently has been reaffirmed by Tomlinson and Hardy looks upon friction as the force existing between the molecules of two surfaces which have been brought within the range of each other's atomic fields. Again, many authorities are not in agreement and it is generally felt that until the nature of molecular forces is much better understood, attempts in understanding friction must be made at the microscopic rather than the molecular level.

Presently, among the most prominent group of theories, is the adhesion or welded junction theory which holds that the initial points of contact are extremely small and are therefore loaded beyond the yield limit. Consequently, plastic flow takes place until contact areas are increased in size and number so that the load can be supported. The plastic flow results in welded junctions of contact and it is the shearing of such junctions which represents the required friction energy to cause tangential motion. Some proponents of this theory hold that the localized temperatures at the load bearing point of contact reach melting temperatures while others believe that this welding is of a cold-weld nature. Those of opposing views hold that the welded junction concept does not match the known and measurable reactions between load bearing surfaces and there are arguments and counter-arguments concerning the forces required to separate two surfaces without tangential motion if welded junctions have occurred upon contact.

The dominant work of Bowden in this field is clearly presented by the following quotation from one of his papers, " Although stress will cause elastic deformation of the metal in the vicinity of the points of contact, experiments suggest that the summits of irregularity on which the bodies are supported flow plastically and are crushed down until their cross-section is sufficient to enable them to support the applied load. The real area of contact A is given by $A = W/P_m$, where P_m is the yield pressure of the metal ".

Of particular importance to the investigation of potentiometer transducers is Bowden's statement, " The fact that the real area of contact is so small has practical implications. Even when loads of *only a few* grams are applied to the surfaces, the local pressure between them may be sufficiently great to cause the flow of metal ". Additionally, Bowden states that, " When large flat surfaces are used, it does not mean that the real pressure is much less, but merely that the

points of contact are more widely distributed. This intense pressure will cause adhesion or pressure welding at the tiny points of contact and so produce small metallic junctions between surfaces ".

The adhesion theory provides a reasonable explanation for the fact that friction is largely independent of surface area, since actual contact area and total surface area are assumed to be independent of one another. It provides the fact that friction is dependent on load since the real area of contact is dependent on load. By experiments, it has been determined that the friction coefficient of most metals is of similar value. Therefore, it follows that the product of area × shear strength will not vary over a large range.

Considerable difficulty is encountered in explaining the performance of cleaned, outgassed surfaces tested under high vacuum. If the actual contact areas are assumed to be welded it is difficult to understand how friction coefficients on first motion can ever exceed the ratio of shear strength to compressive yield strength. For the theories which assume interaction between surfaces which accounts for practically all theories except the Coulomb theory, there is an obvious interest in the nature of the surface layer in terms of oxides, absorbed gases, etc.

Considerable work has been done on the examination of surface characteristics. Wilson and Whitehead, for example, working independently, have shown experimentally that the effect of the oxide layer can be quite different for different materials and that the relative hardness and thickness of the oxide films are the important factors together with surface finish of the base metal. These characteristics tend to fall into three categories.

Typical of the first case is aluminum on aluminum in which the thickness of the oxide coating is insufficient to support even light loads, and penetration of the layer invariably occurs. The effect of the oxide is therefore minimized, and the action is largely dominated by the characteristics of the base metal, thus providing a relatively high coefficient.

Another case can be considered of which Chromium is typical. Here the outside film is not ruptured, even at high loadings and the friction coefficient is largely that of the oxide rather than the base metal.

As would be anticipated, an intermediate category is found to exist (copper/copper) in which, for light loads, the oxides remain intact and a low coefficient is obtained. As load is increased, a region is found in which penetration or failure of the oxide layer occurs. The coefficient of friction increases with load up to a point where the oxide layer is completely destroyed and the coefficient is largely established by the characteristics of the base metal. Wilson has also shown that electrical resistance measurements taken during tests of this nature tend to confirm this interpretation.

Early work in the field of vacuum friction was performed by Hughes in 1939. The pressure inside the vessel containing the samples was held below 10^{-6} Torr. The metal samples were outgassed by heating them in the vacuum, and the friction tests were run when the samples returned to room temperature. For these experiments the metals used were nickel on tungsten and copper on copper. In the vacuum, after the outgassing, the coefficients of friction were seen to increase by a factor of 10 over the coefficients for a clean surface in atmosphere. The increase in the coefficient of friction was considered to be due to the ease with which the metal surface weld together in the absence of contaminant films. The contaminant films (oxide coating, and/or vapor, and other impurities) are usually several molecular layers in thickness when the sample is exposed to the atmosphere. In the evacuated vessel, the samples were found to be contaminated by residual gases from an oil vapor pump, a few minutes after outgassing was performed. A drop in the coefficient of friction was then noted. To study oxide films, traces of oxygen were admitted to the evacuated vessel and it was found that, for the nickel/tungsten combination a reduction of the coefficient of friction took place rapidly.

In 1949, Young performed friction experiments in high vacuum. In these experiments the load between the specimens was increased by a factor of 15 over those loads used by Hughes. Young's experiments were essentially the same as those by Hughes, with care taken to avoid contamination by residual gases. Most specimens used were nickel. After outgassing and at a pressure of 10^{-6} Torr, an increase of the coefficient of friction by a factor of 10 was observed. However, with more thorough outgassing, *seizure* was found to take place, and a coefficient of friction of approximately 100 was estimated. To see the effect of films on friction, oxygen was admitted to the chamber and a gradual decrease in the coefficient of friction was observed. Experiments were performed where hydrogen was admitted to the chamber and no appreciable reduction in the coefficient of friction occurred. Again the experiment supported the belief that the friction was due to shearing of welded metallic junctions.

Experiments were performed in which the temperature was varied. The samples were outgassed and placed in a high vacuum, and the temperature was increased to about 1000 °C. The coefficient of friction was found to vary little at low temperatures, but at high temperatures the coefficient of friction dropped by 50 per cent. The process was found to be reversible, indicating the negligible outgassing had occurred during the experiment. The explanation of the variation of the coefficient of friction follows from the fact that the area of contact between the samples depends on the load and the yield pressure. For the materials tested, at low temperatures the yield pressure decreases, therefore, the area increases for a given load. However, the shear strength drops off so that the force of shear remains approximately constant. At high temperatures, thermal softening occurs while a liquid film forms a substrate under the oxide film.

Experiments on the friction and wear of graphite and other layer latice solids have been carried out by Savage. Savage studied the problem of kinetic friction and wear rate on non-metallic solids (graphite, molybdenum disulphide, boron nitride, mica and diamond), sliding against a clean copper wheel whose peripheral speed was 1000 cm/sec. It was shown that the older explanation of the low coefficient of friction resulting from the intrinsically weak binding forces between lamellae is insufficient for graphite and cannot be applied to diamonds. The graphite sample showed high friction and high wear rate in the vacuum chamber, in contrast to much lower friction and wear rates

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in moist air or water vapor. Low friction and negligible wear rate for MoS_2 occurred in both vacuum and air. BN and mica showed excessive wear in both vacuum and air. These experiments led to the conclusion that sheetlike structure is not alone a criterion of whether a solid substance will act as a lubricant, and that adsorbed films may be required as with graphite.

The findings of these pioneers in the field of friction have been applied to the present requirements of space instrumentation with interesting results.

Considering the major types of transducers in use, the effect of friction is most greatly pronounced in the potentiometer type, because of the force required to overcome static friction as seen by the potentiometer slider arm. Removal of the air bearing in the potentiometer type transducer should cause a high friction effect, not encountered at sea level. Since satellite operation is in the area of 1,500,000 geopotential feet, it is estimated that a vacuum of 1×10^{-11} inches of mercury prevails at this altitude. Satellite operation in the mesosphere will be relatively free of vibration and acceleration, therefore friction effects will become greatly magnified, if high vacuum effects the friction percentage. Loss of the air bearing will also have pronounced effect on the cooling of a transducer. It has been noted that high excitation voltages, (10–12 V) applied to a strain gage, caused burn-out of the gage when submitted 1×10^{-6} Torr (effects of I^2R).

From this study we can only conclude that all existing theories of vacuum friction leave much to be desired.

The Coulomb theory, for many reasons, is considered to be implausible and the molecular theory, as commented, is considered impractical. While the adhesion theory appears to be the most comprehensive and rational concept, there is some difficulty encountered in explaining such points as how a coefficient of friction greater than unity can be obtained for ductile metals having a shear strength less than the compressive yield. The ultimate goal of the Data Sensors investigation is to provide better instrumentation for measurement and control by being aware of the limitations of our present earthbound concepts as applied to outer space environments.

Acknowledgements

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A Leak-free Method of Transmitting Motion into Ultrahigh Vacuum

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A description is given of a seal which is leak-free and can be used to transmit rotary and limited translational motion into ultrahigh vacuum. The seal is accomplished by using a low vapour pressure liquid in combination with a rubber gasket. The seal is useful at 10^{-9} Torr and below and therefore has excellent application for testing of mechanisms, bearings and materials in ultrahigh vacuum. Application of the seal to apparatus for bearing testing in vacuum and to apparatus for tensile testing in vacuum is discussed.

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Introduction

One of the formidable problems confronting the designer of space vehicles is the degrading effects of the vacuum in space on bearings, mechanical mechanisms and materials. Most lubricants are useless in space due to their high vapour pressure. Once lubricants and surface films are lost either by volatilization or as a result of frictional wear, the resulting uncontaminated surfaces may seize and cold weld. In order to test bearings and mechanisms in ultrahigh vacuum, it is generally necessary to pass some sort of sealed rotatable shaft into the vacuum chamber. In addition, metals and plastics exhibit different physical properties in vacuum. A seal capable of providing translational motion in vacuum is often useful for tensile testing of such materials.

An ultrahigh vacuum seal which has been developed for testing of components and materials in a simulated space environment will be discussed and construction details given. This seal permits rotary motion and limited translational motion to be introduced into a vacuum chamber while being leak-free and with no torque or life limitations. When properly designed series cold traps are used in conjunction with the seal, it will operate without difficulty in the ultrahigh vacuum region required by space environment simulation apparatus.

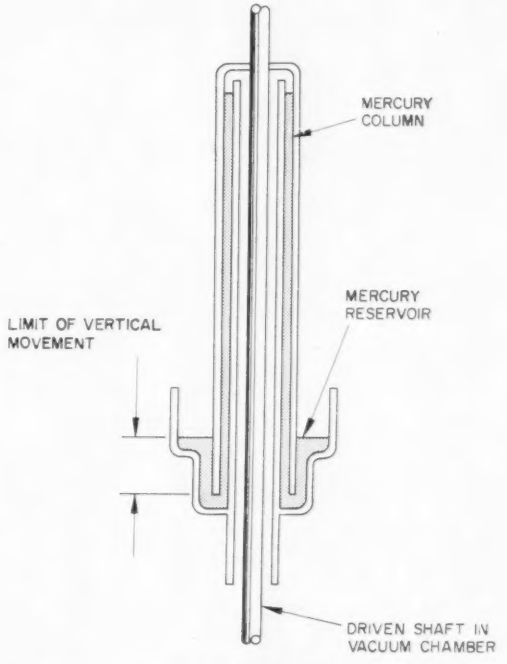

FIG. 1. The most simple form of the liquid seal.

Principle of operation

In the most simple form of the device, a gas-tight seal is accomplished by balancing atmosphere pressure against an equivalent column of low-vapour pressure liquid. The low vapour pressure liquid is held in a stationary reservoir and the rotating shaft is connected to a tube which dips into the liquid. This device, which is shown in Fig. 1, is similar to the common mercury seal which has been used in chemical laboratories for many years. An improved seal similar to the one shown in the figure has been described by Baldridge[1] and uses graphite support bearings. If mercury is used as the low vapour pressure liquid, the column height will be approximately 760 mm when the driven shaft is in vacuum. Liquids less dense than mercury will result in a corresponding increase in column height. By making the reservoir deep, it is possible to produce vertical displacements of as much as several inches while still maintaining the seal.

The mercury seal shown in Fig. 1 is cumbersome due to its being several feet in height and is difficult to support at high rotational speeds. By placing a rubber gasket between the reservoir outer wall and the central tube a chamber is formed. The pressure in the chamber thus formed can be

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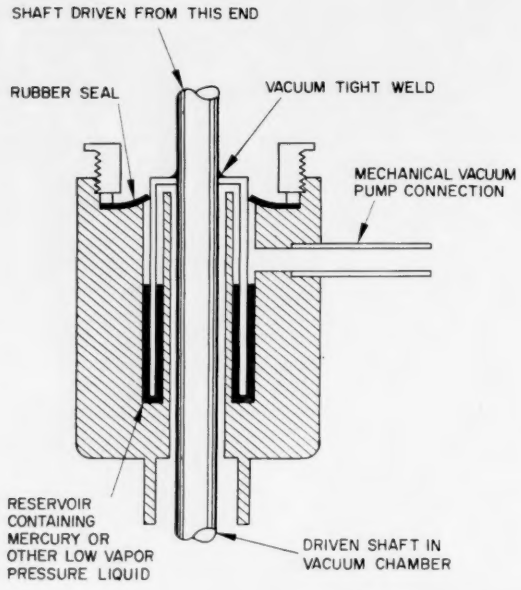
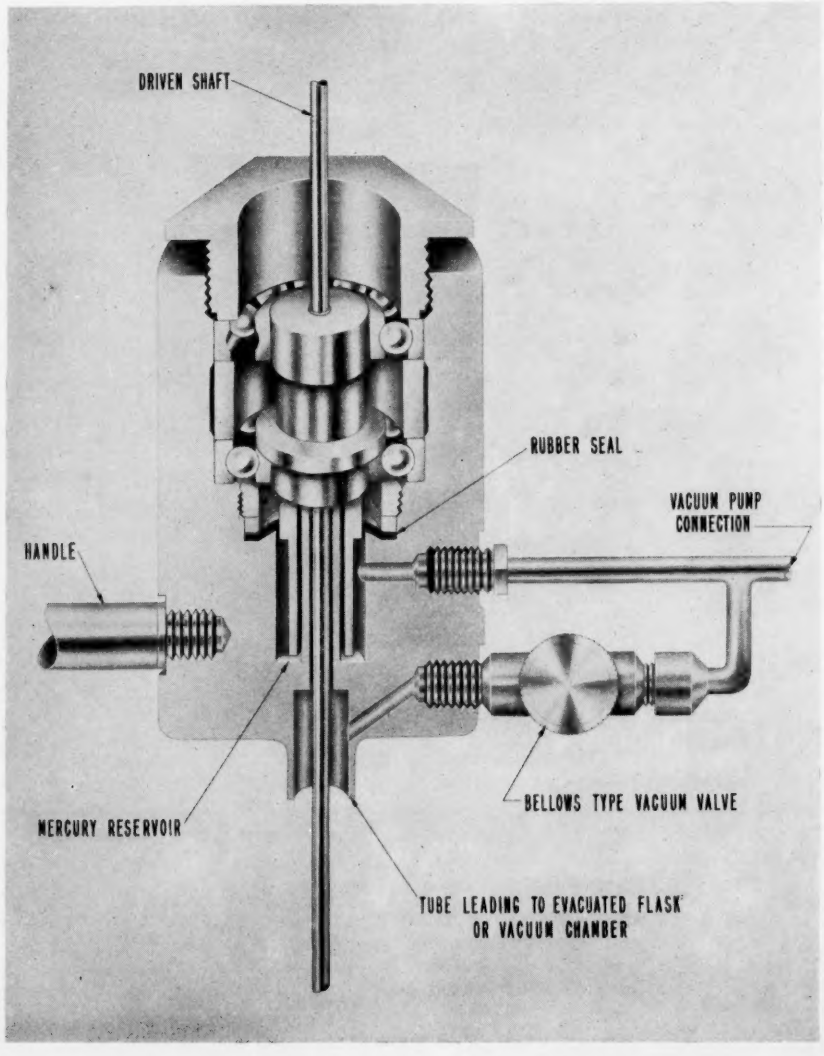

SHAFT DRIVEN FROM THIS END
RUBBER SEAL
VACUUM TIGHT WELD
MECHANICAL VACUUM PUMP CONNECTION
RESERVOIR CONTAINING MERCURY OR OTHER LOW VAPOR PRESSURE LIQUID
DRIVEN SHAFT IN VACUUM CHAMBER

reduced to under 1 Torr without difficulty using a mechanical vacuum pump. Such a modification results in a greatly reduced height for the seal. The appearance of this seal is shown in Fig. 2. For simplicity, no internal support bearings are shown in the figure. The central tube dips into the low vapour pressure liquid permitting limited vertical displacement without loss of the seal. This basic mechanism can be used for rotation in vacuum, rotation in combination with limited translational motion, or translational motion alone. A device, not related to the ordinary mercury seal, has been previously described by the author[2]. This seal, which is designed to enter vacuum chambers from below also uses the differentially-pumped-liquid principle.

FIG. 2 (*left*). Basic mechanism for transmitting unlimited rotational and limited translational motion into a vacuum chamber.

FIG. 3 (*below*). Internal construction of the seal when used to pass a rotating shaft into vacuum.



At room temperature, mercury has a vapour pressure of approximately 1 μ. Some synthetic pump oils have vapour pressures in the 10^{-7}–10^{-8} Torr region. Therefore, to reach ultimate vacuum, this seal must be used in combination with a baffled series cold trap. When using mercury as a seal liquid and if liquid nitrogen is used in the series cold trap, the seal will perform properly at pressures less than 10^{-9} Torr without difficulty. When using mercury, trapping can be easily accomplished as non-condensable decomposition products will not be present.

Construction of a rotary seal

Internal construction of the seal for transmission of rotary motion into a vacuum chamber is shown in Fig. 3. The body of the seal is approximately 4 in. high and is designed to contain about 3 ml of mercury. The rubber seal shown in the figure is similar to that described by Wilson[3] and is made of neoprene rubber. Other types of gaskets such as O-rings or compression seals can be used if desired. The Wilson seal has the advantage that it receives the load of atmospheric pressure and is thus held tightly against the rotating central tube regardless of any permanent set the rubber may acquire.

When the differential pressure between the seal reservoir and the vacuum chamber is more than several centimeters of mercury, the mercury will be pushed up the tube far enough to break the seal and slight splattering of the mercury will occur. This problem arises during initial pumpdown of the seal reservoir and vacuum chamber, and also when the vacuum pump going to the reservoir or the system vacuum pump is turned off. The problem can be readily solved by using the bellows vacuum valve shown in Fig. 3. When this valve is opened, the reservoir and the vacuum chamber are connected together and therefore the pressure on both the mercury surface in the reservoir and that in the chamber will be essentially identical.

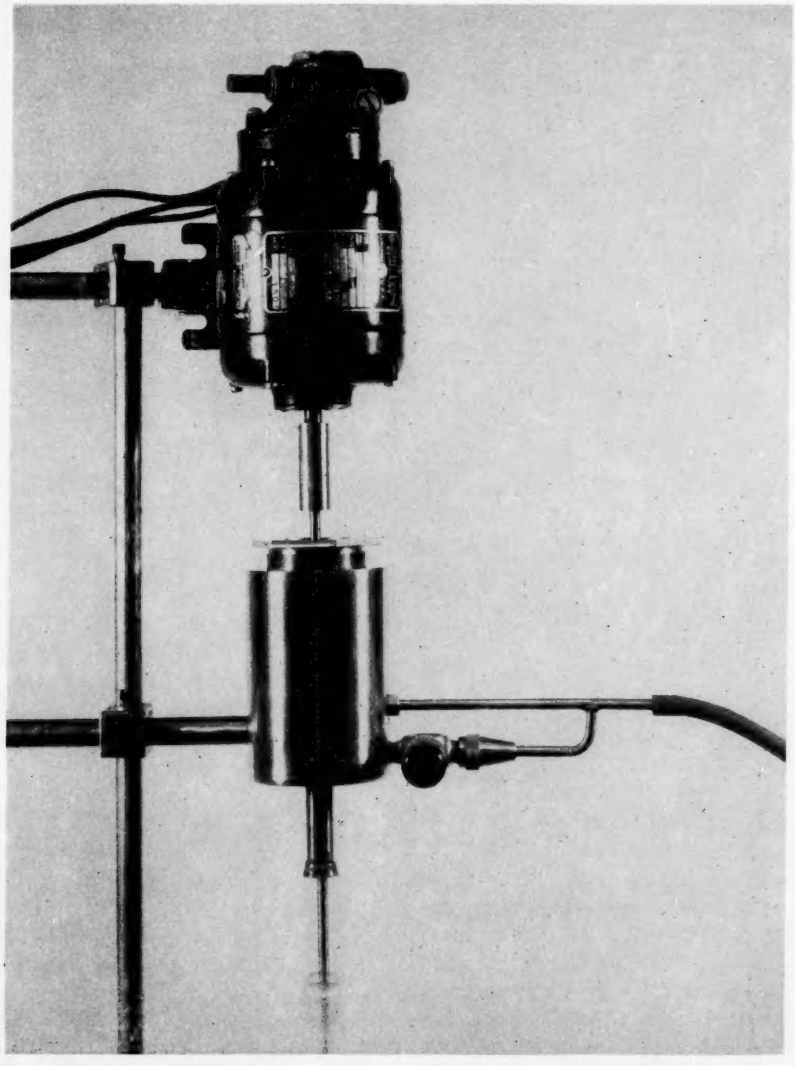


FIG. 4. Rotary seal and drive motor assembly.

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An excellent material for use in construction of the seal is stainless steel and ball bearings can be used to maintain proper centering and to support the driven shaft. Fig. 4 shows the completed rotary seal driven by a small electric motor. The handle which is shown in Figs. 3 and 4 has proven valuable to support the device and removes the strain from the glass tube leading to the series cold trap. A Kovar tube has been welded into the seal shown and a graded glass-to-metal-seal attached to the Kovar. The series cold trap is a Dewar type made of Pyrex. The rubber tubing shown in Fig. 4 leads to a mechanical vacuum pump which has sufficient pumping capability to maintain the reservoir pressure at approximately 150 μ.

Applications

The seal is valuable whenever a driven shaft must be placed in ultrahigh vacuum. One typical application is the testing of bearings or other mechanical devices in ultrahigh vacuum. The general method of assembling the rotary seal into ultrahigh vacuum apparatus is shown in Fig. 5. The

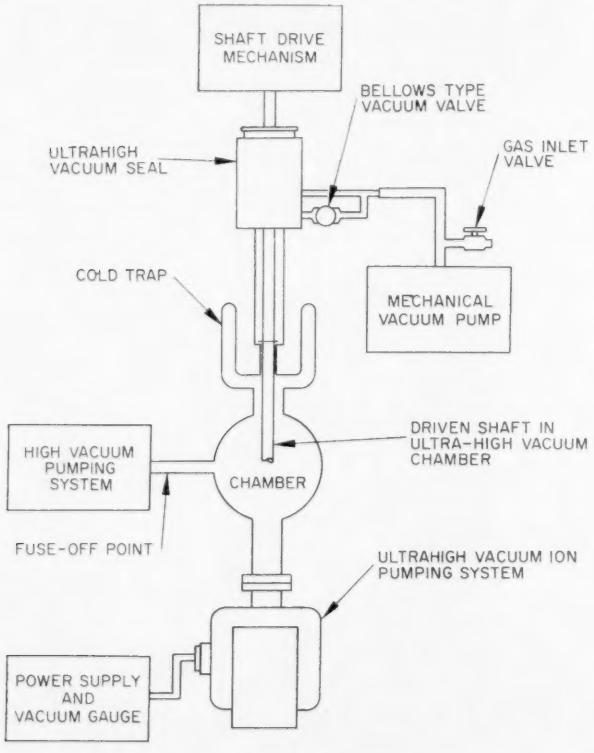

FIG. 5. Ultrahigh vacuum apparatus for use with the rotary seal.

bearing or mechanism to be evaluated is attached to the driven shaft in the vacuum chamber and also to some convenient mounting bracket within the chamber. The apparatus shown uses ion pumping, although other pumping methods can be used. After the device to be evaluated has been installed, the gas inlet valve is closed, the bellows vacuum valve is opened, and the high vacuum pumping system is started. When the pressure in the chamber has fallen to approximately 2 Torr the mechanical pump is started. The bellows vacuum valve may now be closed and the high vacuum pumping system used to pump the chamber to 10^{-4}–10^{-6} Torr. A high vacuum pumping system often used in this laboratory is a three-stage mercury diffusion pump backed by a mechanical roughing pump. Once high vacuum has been reached, the lower portion of the cold trap may be baked out while the system is being pumped by the high vacuum pumping system. The bake-out temperature and time will be governed primarily by the sensitivity of the device being evaluated. Liquid nitrogen should then be placed in the cold trap and the chamber baked for another period of time. As it is necessary to keep the level of the liquid nitrogen constant in the cold trap, an automatic filling device described by Feld and Klein[4] has proven useful. Following this, the ion pumping system should be turned on and the high vacuum system fused-off or valved-off from the chamber so that pumping to ultrahigh vacuum can be accomplished using the ion pump alone. Using the apparatus shown, the rotary seal has been used at speeds up to 4000 rev/min and at pressures to 6×10^{-9} Torr.

When the evaluation has been completed and the ion pumping system turned off, the bellows vacuum valve should be opened to prevent splattering and gas can be bled into the system through the gas inlet valve.

Application of the seal for tensile testing in vacuum can be accomplished using the apparatus shown in Fig. 6. In this

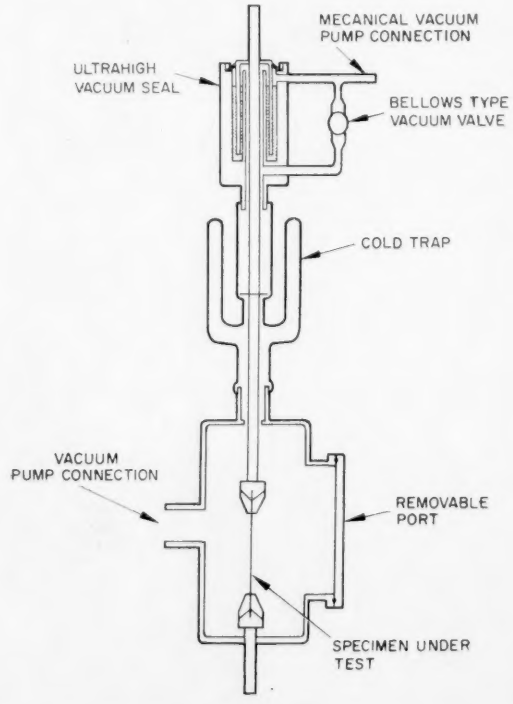

FIG. 6. Application of the seal to a vacuum tensile testing device.

instance the depth of the reservoir is considerably increased so that vertical translational motion of several inches is possible. The shaft going into the seal is attached in the upper jaws of the tensile testing machine and the shaft

below the specimen test chamber is connected to the lower jaws. A removable port should be attached to the test chamber to facilitate assembly and removal of the test specimen. This port may have an integral window for observing the experiment or for applying external radiations such as infrared and ultraviolet light. Depending on the diameter of the tube upon which the rubber gasket slides, the device will receive a constant downward load due to atmospheric pressure when the chamber is evacuated. Therefore several calibration runs of the apparatus should be made using no specimen in the chamber. The constant downward force due to atmospheric pressure and also the seal friction, can then be taken into consideration.

If experiments in the 10^{-7} Torr region are contemplated, the cold trap can be eliminated and a low vapour pressure pump oil used in the ultrahigh vacuum seal. The chamber should be constructed of metal to reduce implosion hazards. When using the series cold trap, the ultrahigh vacuum seal should be rigidly fixed with respect to the vacuum chamber to prevent damage to the trap.

It goes without saying that these applications are only examples of a variety of possibilities where the seal can be used to advantage. Due to its complexity this seal is valuable mainly for ultrahigh vacuum systems where a high level of sophistication is required.

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The Adsorption of Water on Tungsten

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The adsorption of water on tungsten using a field emission microscope at 80°K, room temperature and 400°K is described. The field was found to effect the rate of surface migration and mode of adsorption on particularly the (001) region of the point emitter. The desorption of water was also studied and found to be dependent on the history of adsorption.

1. Introduction

In the study of adsorption processes it is desirable to start with an atomically clean surface so giving a reference state. The field electron microscope (hereafter known as f.e.m.) is one of the few instruments capable of demonstrating unequivocally atomically clean surfaces, albeit for a few metals. The microscope consists of an electron tube, similar to a cathode ray tube in design, capable of being evacuated to pressures of 10^{-9} Torr (and better) but with a different type of cathode assembly. The cathode consists of a support loop and a very fine emitter tip. When a high potential (4–20 kV) is applied to the anode, fields of the order of 10^7 V/cm are produced at the emitter surface, and field emission of electrons occurs. On striking the phosphor screen, forming part of the anode assembly, a pattern is produced (Fig. 1a) which is a work function map of the emitter surface.

Due to the drawing process in the fabrication of tungsten wire there is a preferential orientation of the crystal planes with the (011) plane appearing perpendicular to the drawing axis. The centre of the picture will show this (011) plane and if the hemisphere of tungsten is projected the diagram in Fig. 1(b) is obtained which serves as a key to the f.e.m. patterns. This is possible because the end diameter of the tip is a few thousand Ångstroms and thus the observed surface forms part of a single crystal, whose various crystal

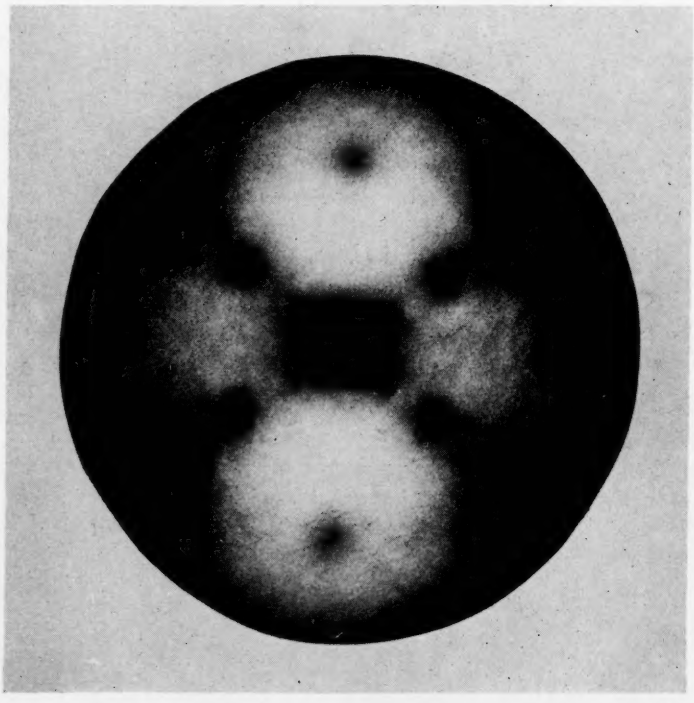

FIG. 1(a). Clean tungsten.

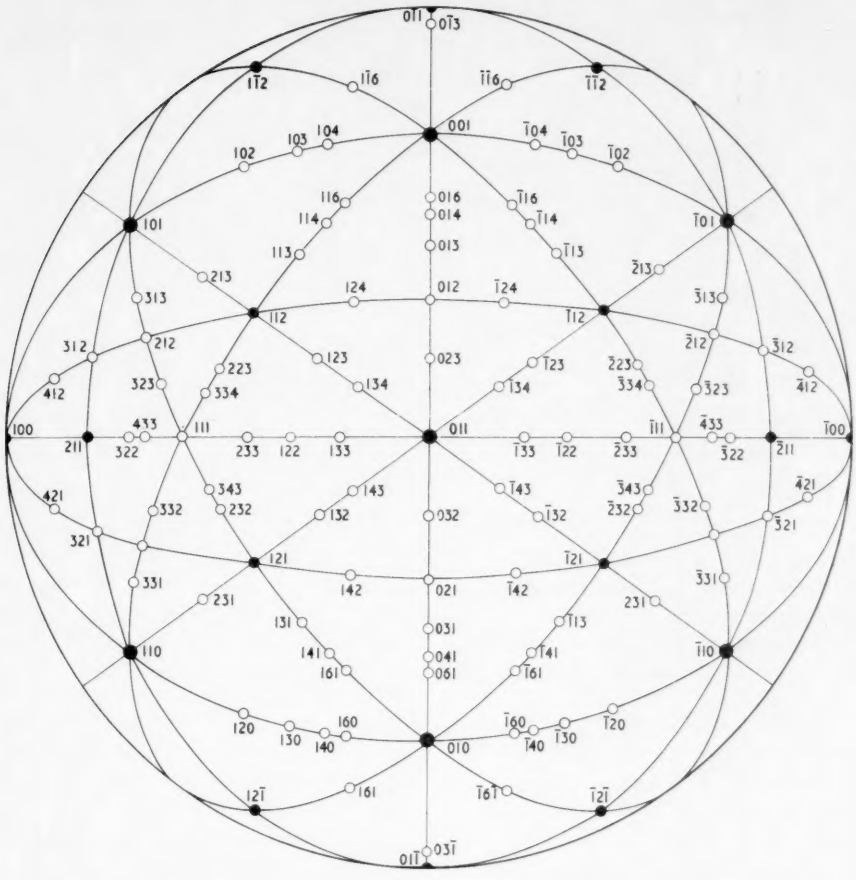

FIG. 1(b). Crystallographic projection—diagram of a tungsten single crystal hemisphere.

planes form part of the tip surface. The emitted field electrons from these planes are projected as a pattern on to the screen and appear as differences in light intensity due to their differences in work function, as seen in Fig. 1(a).

Water forms a large proportion of the residual gases found in glass ultra high vacuum tubes before gettering[1, 2]. It is important to know what reactions the water vapour will have with any metal filaments and what effect any applied field which may be present in thermionic or controlled thermonuclear devices will have. A f.e.m. was used to study the effect of water on a fine tungsten point.

Little work has been done on the effects of water on hot filaments. The small amount of data available indicates that water is probably desorbed as hydrogen leaving an oxide layer at temperatures around 1000–1500 °K[1, 3]. This reaction has been studied in greater detail together with the effect of the applied field (of the order of 10^7 V/cm) on the adsorbed layer of water in this laboratory. It has been reported that this field changes a layer of adsorbed oxygen or carbon monoxide[4, 5]. This change was attributed to a surface diffusion of the ad-layer as polarized ad-atoms or ad-mols tending to move to positions of least free energy and if in the course of this diffusion the adsorbate should meet the hole sites found around (001) planes it will be trapped there. It was interesting to note the effect of an applied field on an adsorbate and how the observed surface in a f.e.m. compared with the surfaces of bulk adsorbents. The effect of the field on diffusion and desorption processes has been recently reviewed by Becker[6] and the increase in rate of reaction is attributed to a change in the bond strength between surface atoms and substrate due to the applied field.

Using the flash filament technique[7], Ehrlich[8] has shown that for the gases nitrogen, and carbon monoxide adsorbed at room temperature two distinct desorption peaks appear for increasing temperature. That two distinct binding states for oxygen exist has been known for some time[9] and two states for hydrogen have been reported[10].

2. Experimental

The details of construction of the f.e.m. are fairly well established. Suffice to say, the microscope tube was designed so that the tip could be cooled by liquid nitrogen by having the end piece in the form of a bent dewar flask (see Fig. 2). The temperature of the tip was estimated by the method due to Gomer[11], by using subsidiary potential leads spot welded to the main supporting hair-pin the resistance of the small

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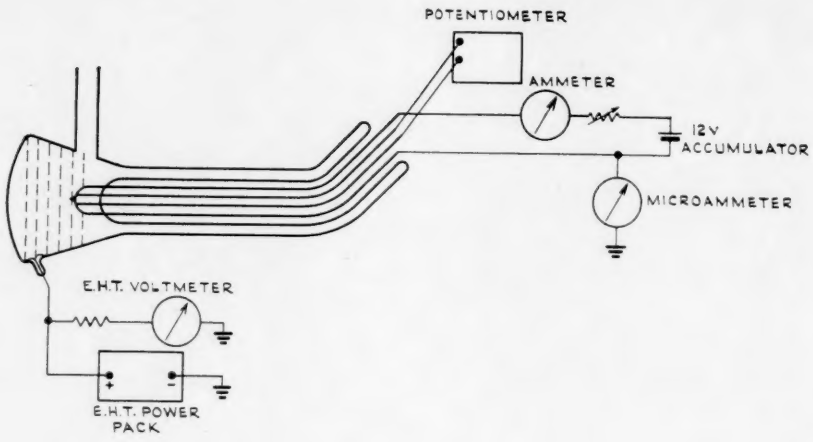


FIG. 2. E.H.T. circuit.

centre portion was measured (see circuit diagram Fig. 2). From the values of the resistivity the temperature of the middle portion could be calculated.

The microscope tube was evacuated to pressures of 10^{-10} Torr or better using standard ultra high vacuum techniques. A few millilitres of distilled water were introduced into the gas-dosing part of the system and carefully outgassed. The water was frozen, pumped and then melted repeatedly, to remove, as far as possible, all traces of dissolved air. The water vapour was admitted to the f.e.m. via a ceramic leak before an experimental run, and precautions were taken to flush the system well before an adsorption was observed. The screen of the f.e.m. was photographed using a Shackman auto-camera MK III with a f 3.8 lens and using HP3 film ; an exposure of 1/10 sec and one of 1/25 sec were taken for each step in the adsorption sequence and for each flashing temperature in a desorption, so that a complete record could be kept. This was necessary as differences in contrast are continually lost, first at the phosphor which is unable to accommodate all intensities of electrons in a f.e.m. pattern, and secondly in the film which cannot cope with the range of brightness on the screen.

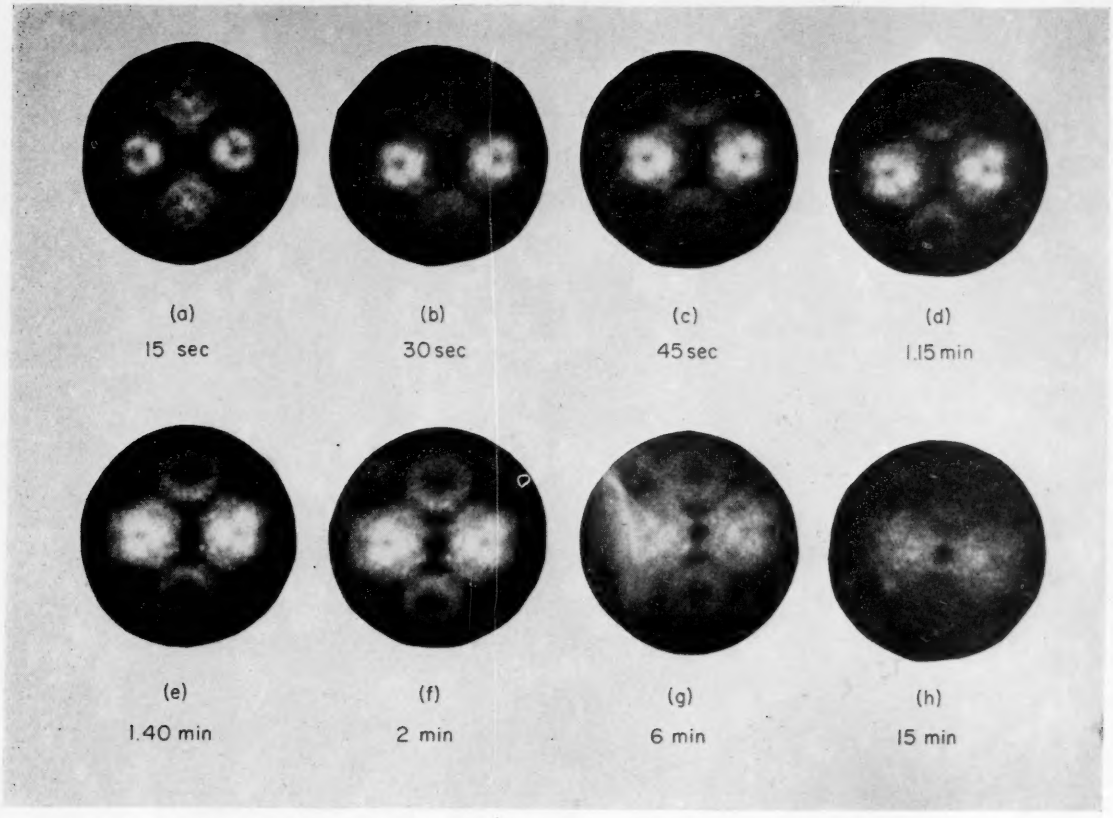
3. Results and discussion

The sequence of events of the adsorption of water by tungsten at room temperature and fairly high pressure for f.e.m. working is recorded in Fig. 3. Since rather lengthy precautions had been taken to ensure that the residual gas contained as high a percentage of water as possible, adsorption at low pressures was impossible. In Fig. 3(a), only 15 sec after a high temperature desorption flash, a considerable amount of adsorption had taken place, principally on the rough areas of the tip surface around the (111) and (001) planes. The adsorption of water at this pressure of 1.6×10^{-7} Torr was extremely rapid and after 15 sec increase in emission from around the (112) planes denotes that second layers[15, 16] of water have already formed on the steps surrounding these planes. The adsorption then proceeds in Fig. 3(b) when the (023) planes which lie above and below the central (011) plane darken as water was adsorbed. After 1 min 40 sec in Fig. 3(e) the remaining (023) planes darken to form a ring around the two (001) planes. The process of adsorption in the (001) area continues until after 15 min the whole area had a very high work function and appeared very dark on the screen.

Meanwhile, in the (111) area, after the initial attack of the (111) plane itself which stood out as a black dot in Figs. 3(a–f), the whole area is gradually covered by a monolayer which was indicated by a general increase in work function and darkening of the area. The interesting fact was that the (111) plane appeared to have a marked affinity for the adsorption of water vapour (in contract to CO and O_2 adsorption). After 15 min at this pressure or 1.4×10^{-4} mm sec it was noticed that the beginnings of "build-up"[12–14] could just be seen in the (111) area at about the (233) plane showing as points of high emission. This effect which does not occur with pure oxygen until 1200°K[14], is caused by the migration of W atoms under adsorbed layer due to the increase in field strength as a result of adsorption[12–14]. The increase in field strength due to adsorption of water must therefore be greater than that for oxygen. This build-up effect was more marked at higher temperature adsorption as will be seen later.

Although second layers of ad-mols form initially around the (112) planes, as shown by halos of emission around these planes, after 3 min these have disappeared and the material adsorbed here probably diffuses over the first layer to areas where adsorption is still less than monolayer, i.e. the (001) plane.

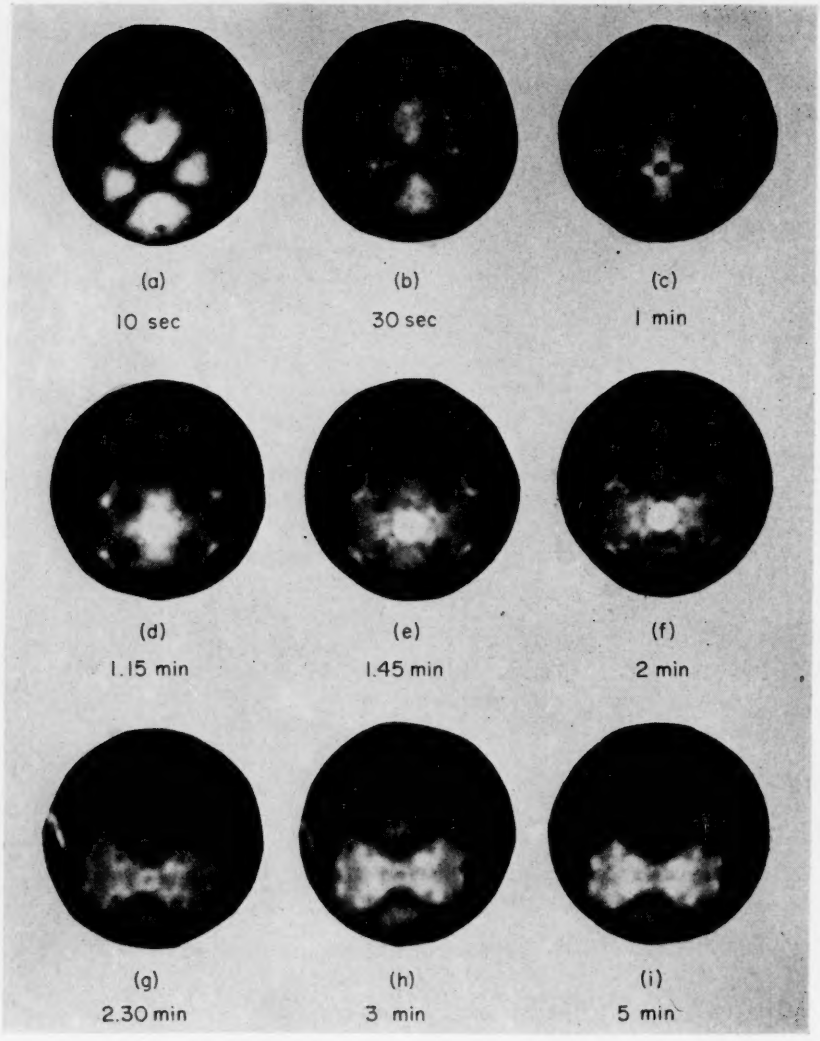
A run was also made at a lower pressure, viz. 2.8×10^{-8} Torr, but the gas in the system may not have contained such a high percentage of water vapour, as the flushing process was not so extensive as in the high pressure run. However, this run confirmed the previous results obtained by Hill and Jacobs[3] in which water was introduced from a side arm just outside the baking oven containing water cooled to liquid nitrogen temperature. This run is shown



	f 5.6	Exposure 1/10 sec	
	kv	μA	mm × 10^{-7}
(a)	16.2	1.8	1.6
(b)	16.3	1.9	1.6
(c)	16.3	1.8	1.6
(d)	16.3	1.7	1.6
(e)	16.9	2.0	1.6
(f)	17.0	2.1	1.6
(g)	17.0	2.9	1.5
(h)	18.0	2.7	1.5

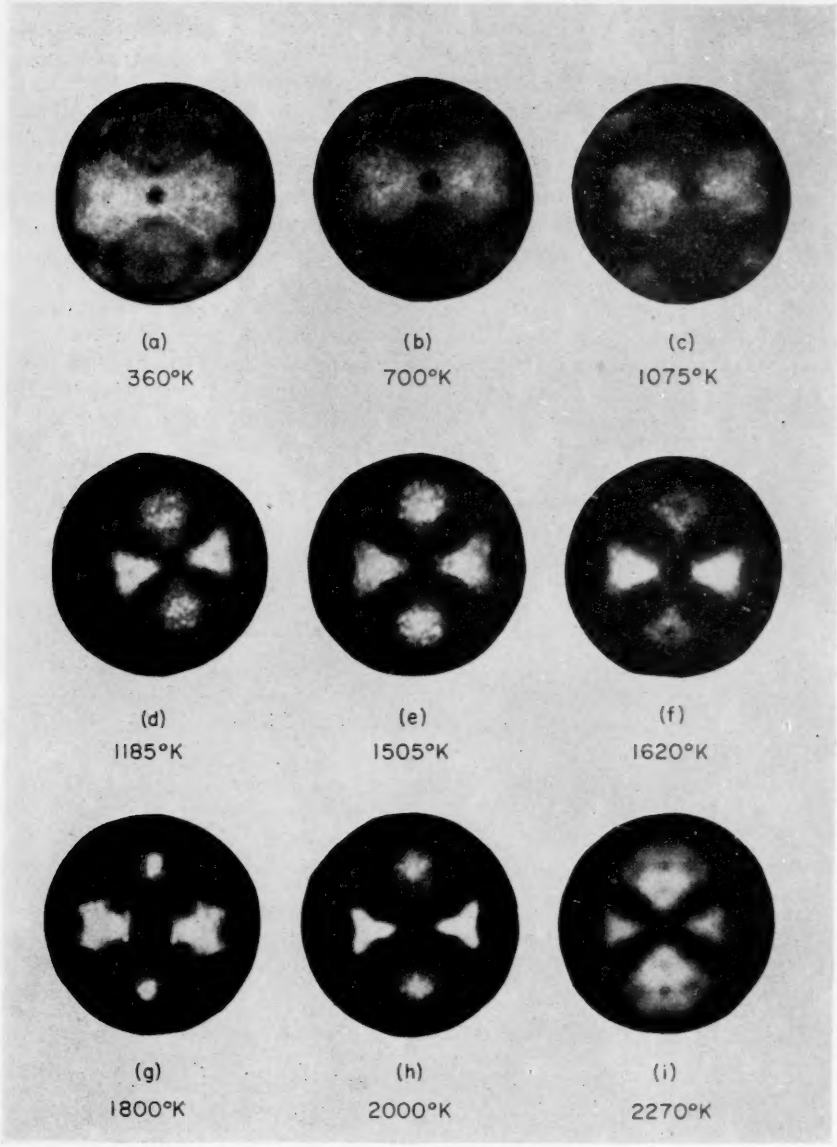
FIG. 3. Adsorption of water at high pressure at room temperature.

in Fig. 4. The main contrast between this and the high pressure run is that second layer adsorption took place on the steps around the (011) planes before attacking the (112) planes ; whereas it was the (112) plane steps which were the first to adsorb second layers in the high pressure run. Fig. 3(a) which shows adsorption at 2.4×10^{-6} mm sec should compare with Fig. 4(d) which shows adsorption at 1.7×10^{-6} mm sec. Clearly these photographs of the f.e.m. pattern do not compare very well, but at this stage it should be noted that in Fig. 4(d) the surface has been under the influence of the applied field for 75 sec whereas in Fig. 3(a) for only a few seconds. The final stages of adsorption at low pressures however, compare quite well, viz. Figs. 3(h) and 4(i), where the very dark high work function area of the (001) and vicinals is apparent. It seems, therefore, that the field affects the adsorption of water by redistributing the



	f 5.3	Exposure 1/10 sec	
	kV	μA	mm $\times 10^{-8}$
(a)	7.5	0.6	2.8
(b)	9.0	1.5	2.8
(c)	9.5	1.7	2.8
(d)	10.0	2.3	2.8
(e)	10.5	3.9	2.8
(f)	10.4	3.2	2.8
(g)	10.5	4.8	2.8
(h)	11.0	3.9	3.2
(i)	11.5	4.8	3.2

FIG. 4. Adsorption of water at low pressure at room temperature.



	f 5.6	Exposure 1/10 sec	
	kV	μA	mm × 10^{-9}
(a)	15.8	2.04	19.0
(b)	16.8	2.7	9.1
(c)	16.2	2.4	6.1
(d)	15.9	2.6	6.1
(e)	15.2	2.2	5.0
(f)	14.8	3.7	4.8
(g)	14.9	5.1	4.8
(h)	15.0	4.1	4.8
(i)	12.0	0.72	5.0

FIG. 5. Desorption of water adsorbed at room temperature.

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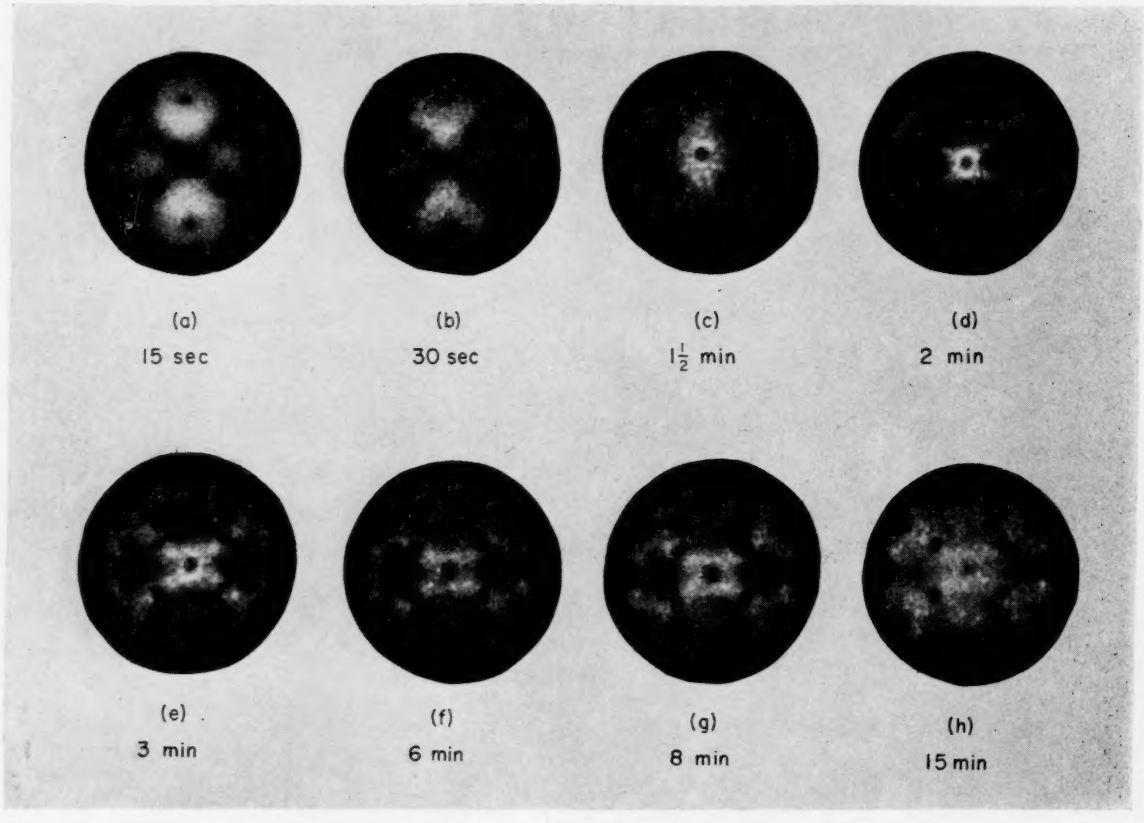
ad-layer over the surface in the early stages of adsorption.

Fig. 5 shows the results of heating the water covered tip to the temperature indicated for each picture for 2 min with the field turned off, and immediately turning on the field and photographing. Fig. 5(a) is the tip with adsorbed water depicted in Fig. 3(h) after pumping to 3×10^{-8} Torr and with an increased applied field. After flashing at 600°K in Fig. 4(b) material has started to be desorbed from the (112) planes and the (001) area was attacked giving a granular appearance. " Build-up " is starting to become evident in Fig. 5(e) in the (111) region and during the desorption flash at 925°K the ion gauge measured gas being desorbed. During this flash the (001) area has shrunk a little with a clearly defined boundary. In Fig. 5(d) the dark area which covered the (001) plane has completely been desorbed leaving an area covered by oxide and very granular. The " build-up " in the (111) area was not very intense and the (111) planes themselves are apparent as dark spots indicating that the adsorbed species are still held strongly even after a flash of 1130°K. In Fig. 5, the " build-up " in the (111) region is now becoming intense (this contrasts with the desorption of oxygen where a built-up pattern first becomes evident at 920°K) and also the (001) area is intensely emitting and granular. General desorption, probably of hydrogen, continues in Fig. 5(f) until at 1800°K in Fig. 5(g) a pattern is produced which compares exactly with that of the desorption of oxygen (although the temperature to produce this pattern from an oxygen-covered tungsten surface is only 1370°K). The clean-up of the surface then proceeds until a clean surface is produced in Fig. 5(i) in an exactly similar fashion to that of oxygen clean-up.

It is likely that on adsorption in the monolayer, water dissociates as does hydrogen, nitrogen and oxygen. Since the " build-up " evidence shows that the surface potential for the water film is higher than that of oxygen (surface potential = −1.91 V[15]) or hydrogen (surface potential −0.65 V[16]), the water must dissociate into hydrogen and a hydroxyl ad-species and not hydrogen and oxygen. Between



	f 5.6	Exposure 1/10 sec	
	kV	μA	mm × 10^{-9}
(a)	12.0	2.1	9.1
(b)	12.0	2.1	9.1
(c)	13.0	0.9	9.1
(d)	13.8	1.08	9.1
(e)	14.6	1.2	9.1
(f)	15.0	1.25	9.1
(g)	15.1	1.2	9.1
(h)	15.3	1.2	9.1

FIG. 6. Adsorption of water at 80°K.

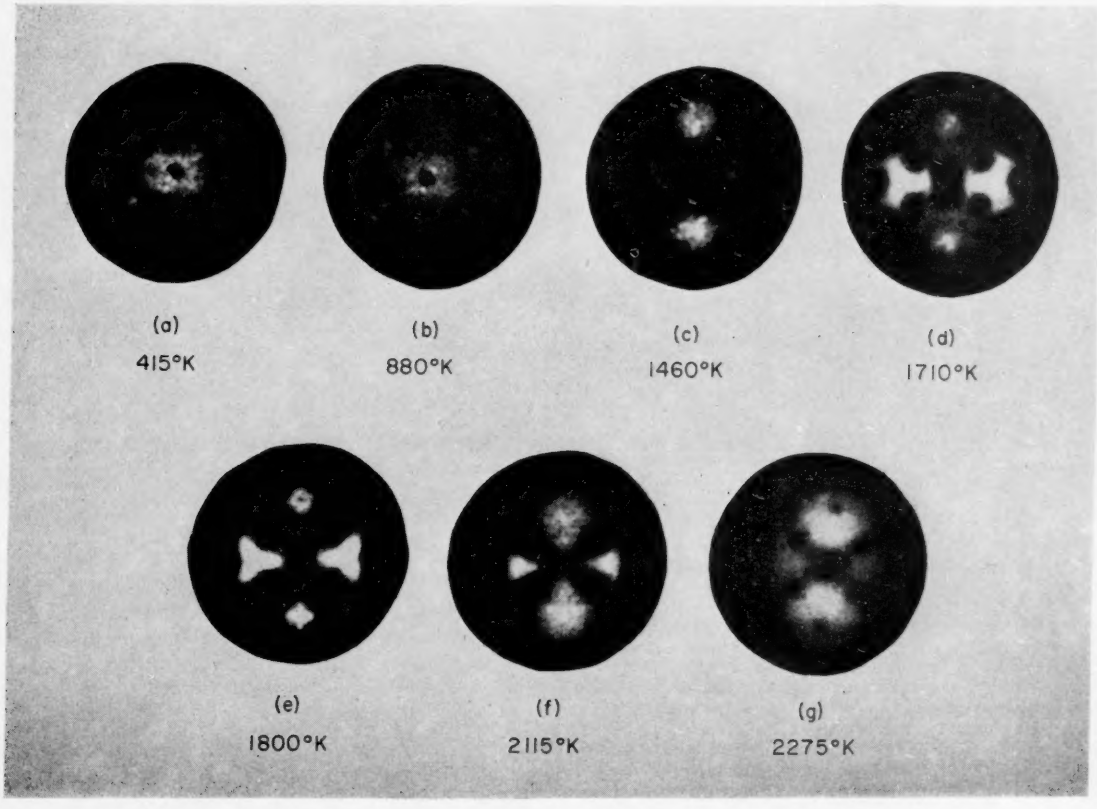
700°K and 925°K gas was desorbed which presumably was hydrogen since a pure hydrogen covered surface also cleans up in this range. Between 1000 and 1695°K the remaining hydroxyl groups probably dissociate and hydrogen is probably desorbed leaving an oxygenated surface indicating that the W–O bond strength is high, comparing with the work of Hanamura[17]. Finally the oxygen leaves the surface between 1700°K and final clean up, as the trioxide trimer, $(WO_3)_3$[18].

$$\text{W}\text{---}\text{O–H} \xrightarrow{700\text{–}925\,^\circ\text{K}} \text{W}\text{---}\text{O–H} + \tfrac{1}{2}\text{H}_2$$
$$\text{W}\text{---}\text{H} \longrightarrow \text{W}$$
$$\text{W}\text{---}\text{O–H} \xrightarrow{1000\text{–}1695\,^\circ\text{K}} \text{W}\text{---}\text{O} + \tfrac{1}{2}\text{H}_2$$
$$\text{W}\text{---}\text{O} \longrightarrow (WO_3)_3\,(\text{g})$$

Although " build-up " was observed even during the late stages of adsorption but in a rather more specific manner than in oxygen desorption, the " build-up " which completely covered the (111) region (i.e. typical of an oxide layer) occurred at a higher temperature than for an oxygen desorption which seems to indicate an activated process. This process presumably is the complete removal of the remaining hydrogen from the adsorbed hydroxyl groups finally yielding an oxide covered (111) surface at 1695°K. The build-up during adsorption occurs in the (111) area on the (122) planes nearest the central (011) plane and not on the ones near the corner (011) planes. This is the region of highest field and the build-up process must be field enhanced and due to the presence also of ad-layers other than oxygen alone. Future work using an omegatron mass spectrometer should resolve the nature of the gas desorbed in the various temperature ranges.

Adsorption of water at 77°K and desorption

The adsorption of water on a tungsten field emitter cooled by liquid nitrogen is shown in Fig. 6. Since the tip was cooled by conduction along a few centimetres of tungsten rod and then the supporting loop wire it is probable that, since the walls of the f.e.m. were at room temperature, radiation from these walls will have kept the tip at a few degrees above 77°K[18].



	f 3.5	Exposure 1/10 sec	
	kV	μA	mm × 10^{-9}
(a)	15.4	1.4	4.3
(b)	15.0	1.2	4.5
(c)	12.0	1.25	4.5
(d)	12.2	3.1	4.6
(e)	12.5	4.0	4.7
(f)	10.2	2.3	4.7
(g)	10.0	2.7	4.7

FIG. 7. Desorption of water adsorbed at 80°K.

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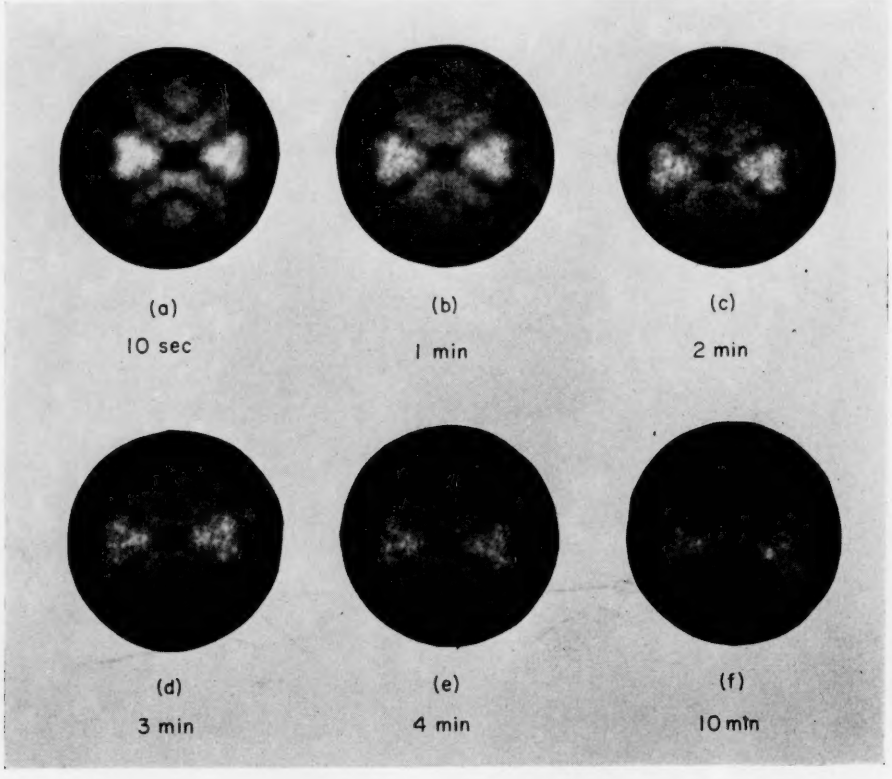
Adsorption in the initial stages compares well with the low pressure adsorption of water at room temperature shown in Fig. 4. Adsorption occurred first on the (001) area and on the (011)–(112) zone lines. Very soon at this low pressure of 9×10^{-9} Torr second layer adsorption was apparent as an emitting ring around the central (011) plane in Fig. 6(c). After 2 min in Fig. 6(d) this trend was extended and second layers of water appeared around the (011) planes and extend along the (011)–(112) zone lines. The intense second layer adsorption was generally spread over the surface as the sequence Figs. 6(a–h) shows but this cannot be ascribed to general overall formation of a second layer as the field to produce emission is constantly increasing during this sequence. It appears that as in the adsorption of water at room temperature, water has a very high sticking probability on the edges and steps surrounding the (112) and (011) planes, but when second layers are formed, these are able to diffuse over the surface of the first layer and deposit on clean areas of the surface. It appears that the activation energy for diffusion within the monolayer is prohibitively high even at room temperature on most planes (cf. CO on tungsten)[19].

In contrast to adsorption at room temperature however the (001) region does not darken appreciably compared with the rest of the surface showing that although surface diffusion can take place, the activation energy for this particular type of adsorption is too high at liquid nitrogen temperature. It was also noted that the overall rate of adsorption is 2–3 times faster at this temperature compared with room temperature.

The tip was flashed until a clean surface in Fig. 7, was obtained. The temperatures quoted are estimates obtained from a curve of resistance vs. temperature since the normal calibration is obtained from room temperature and in this desorption the ambient is about 80°K. The desorption follows reasonably well that of a surface with water adsorbed at room temperature after Fig. 7(c).

The effect of applied field on water adsorbed on tungsten

Preliminary work showed that although the final surface of a tungsten emitter after adsorption[4] is the same, the field applied to obtain emission alters the mode of adsorption. The field may be applied with either polarity to produce the same effect ; the effect is not reversible. It has also been



	f 5.6	Exposure 1/10 sec	
	kV	μA	mm × 10^{-7}
(a)	14.1	1.7	2.5
(b)	14.7	1.86	2.5
(c)	15.0	1.9	2.5
(d)	15.0	2.4	2.3
(e)	15.0	3.3	2.3
(f)	15.6	3.7	2.2

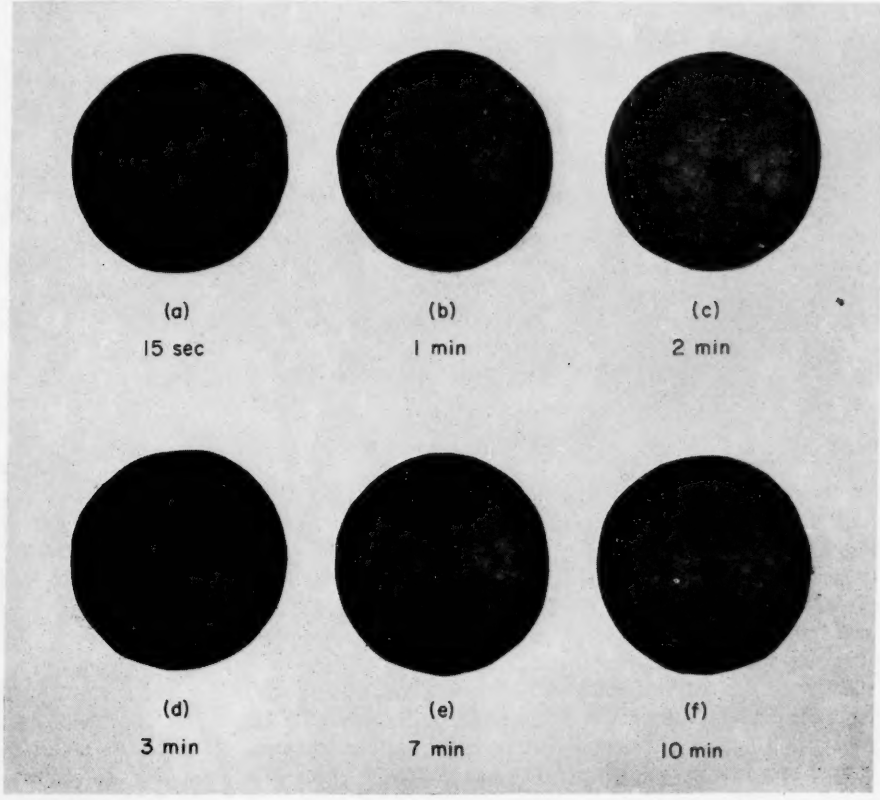
FIG. 8. Effect of field on adsorbed water at 80°K.

observed that in the final stage of adsorption with water vapour at room temperature which is characterized by the darkening of the (001) area, this darkening took place in the absence of a field but only after 2 hr at 3.6×10^{-9} Torr.

In Fig. 8 a tungsten emitter was cooled with liquid nitrogen, and after flushing with water vapour at 2.6×10^{-7} Torr the tip was flashed and water adsorbed in the absence of a field for 29 min. Fig. 8(a) shows the f.e.m. pattern 10 sec after turning on the field. The pattern is similar to that produced by a high pressure adsorption at room temperature (cf. Fig. 3a). After only 1 min the fine structure of the surface has been lost presumably by field induced surface migration. A suggestion that the field enhances the rate of adsorption from the gas phase at this stage must be refuted, since clearly a monolayer is present in Fig. 8(a) and to produce a change from Fig. 8(a–b) in 50 sec at this pressure would require an enormous increase in sticking probability.

In Fig. 8(b) the change seems complete, for even after 10 min (Fig. 8f) the pattern is no different to Fig. 8(b). The lack of any change after 1 min is reflected in the applied voltage and electron current readings which also show no change (the high value for the voltage in Fig. 8(f) is due to the spurious emission clearly visible in the photograph). Although a rearrangement of the adsorbed specie takes place, the darkening of the (001) area is not apparent. It appears that, as in the adsorption with the field applied at liquid nitrogen temperature (cf. Fig. 6), the activation energy for this process on the (001) region is too high at these low temperatures.

A completely different state of affairs occurs when, as depicted in Fig. 9, water was adsorbed by the tungsten tip at room temperature in the absence of a field and the effect of the applied field observed. Fig. 9(a) shows the pattern obtained on applying the field after adsorption for 30 min at 2×10^{-8} Torr with no field applied. The pattern once more is similar to that produced by a high pressure adsorption at room temperature with a continuous applied field. A rearrangement occurred after 2 min (Fig. 9c) especially in the (111) region similar to the one at low temperatures, but then the process continued so that a darkening of the (001) region occcurred after 7 min (Fig. 8e) and was complete after 10 min (Fig. 9f).



	f 5.6	Exposure 1/10 sec	
	kV	μA	mm × 10^{-8}
(a)	14.8	2.04	2.0
(b)	14.8	2.04	2.0
(c)	14.9	2.04	1.8
(d)	14.9	1.7	1.8
(e)	15.2	1.8	1.6
(f)	15.2	1.8	1.6

FIG. 9. Effect of field on adsorbed water at room temperature.

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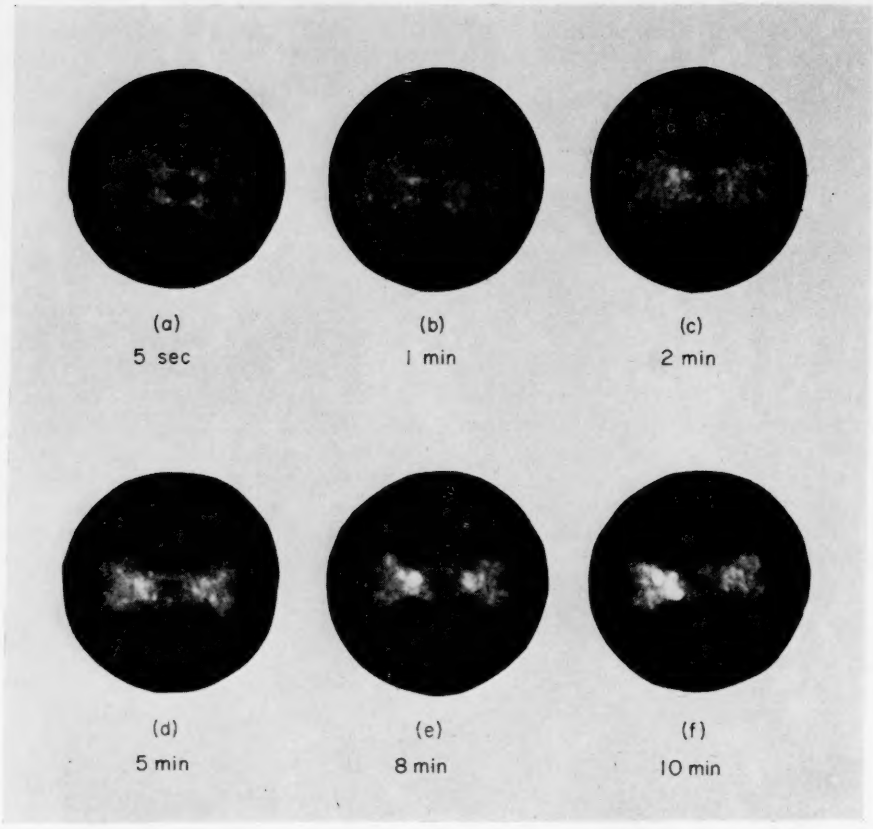

	f 5.6	Exposure 1/10 sec	
	kV	μA	mm × 10^{-7}
(a)	10.0	2.2	2.4
(b)	10.4	1.8	2.4
(c)	10.9	2.1	2.4
(d)	11.1	2.1	2.4
(e)	11.1	2.1	2.4
(f)	11.1	2.3	2.4

FIG. 10. Effect of field on adsorbed water at 400°K.

When water vapour was adsorbed by the emitter held at 400°K for 20 min at 9.8×10^{-7} Torr in the absence of a field, the effect of the applied field is recorded in Fig. 10. Before the field was applied and during the last minutes of adsorption the supply of water vapour was stopped and the microscope tube was pumped down to a pressure of 2.4×10^{-7} Torr. Fig. 10(a) shows the effect of the field after 5 sec applied field, with the (001) region already very dark. The darkening proceeded until after 8 min in Fig. 10(e) only the (111) area was emitting. An interesting feature in this run was that after 5 min in Fig. 10(d), the (111) area appeared very active and gave the impression of " build-up ". This impression was confirmed in Fig. 10(e) after 8 min when a bright spot appeared on the (111) area and finally this area was clearly in the process of " building-up " after 10 min in Fig. 10(f). In the eleventh minute, " build-up " of the (111) region due to migration of the tungsten substrate atoms into ridges was so intense that the tip failed due to a vacuum arc. " Build-up " also occurred with the adsorption of water at room temperature to a small extent as was recorded in Fig. 3(h). It appears that the field due to the adsorbed specie which causes this " build-up " to occur, is stronger for water adsorbed on the surface than for oxygen since when oxygen itself is adsorbed on a tungsten emitter no evidence of " build-up " is found until temperatures of 1200°K are reached as was evident in the desorption experiments. It appears that the field affects the adsorbed layer in two ways. Firstly, by a spreading of the ad-layer over the surface generally which occurs at all temperatures above liquid nitrogen and secondly by increasing the amount of material adsorbed on the (001) region at higher temperatures. Ehrlich[8] has found two main adsorption states for gas adsorbed on tungsten by flash filament techniques, which he designated the α and β states. He shows that the relative amounts of α and β states are dependent on the fine structure of the surface and also that for oxygen the α state is weakly held and is desorbed in the 500°K region whereas the strongly held β state is desorbed in the 1350–1800°K range. There

is a relationship between the two binding states in that the greater the concentration of the β state the lower the temperature of desorption of the α state.

Gomer[20] and Eisinger[21] point out that there are two different adsorption sites available in the (001) region notably on the (113) planes which are stable surface planes for bulk tungsten[22]. These sites consist of essentially holes surrounded by four tungsten atoms and the ridges which will have sites with two nearest neighbours of tungsten atoms. Thus a fully saturated surface will consist of adsorbed material strongly held in holes[18] and less strongly held on the ridges surrounding these holes. On a surface like the (113) plane it is therefore difficult to know what is meant by a monolayer. Although the ad-layer will be staggered the atoms or molecules on the ridges cannot be considered as a proper second layer since they are not directly above the atoms or molecules of the ad-layer in the hole-sites and so reversal of the sign of the surface potential may not occur.

An explanation of the darkening of the (001) area is that this area saturates by surface diffusion and both the hole and ridge sites are filled. The concentration of adsorbed species in the mono-layer is therefore higher than on a close packed plane and the surface potential will therefore be increased to values greater than those on close packed planes. Mignolet[15] has shown that for chemisorbed monolayers this surface potential is usually negative and this ties in with observed decrease in electron emission from the (001) area in the f.e.m. work.

The field affects the adsorbed layer in the following way. The chemical potential μ of the adsorbed layer can be described thus[18].

$$\mu = \mu_{F=0} - \tfrac{1}{2}\alpha F^2$$

where α = polarizability
F = effective field on adsorbed layer
$\mu_{F=0}$ = Potential at same temperature and concentration but zero field.

The applied field will reduce the effective field F and the chemical potential rises due to an increase of $\frac{1}{2}\alpha F^2$ in the binding energy[23]. Thus in the presence of the applied field ad-species will tend to move to places of lower effective field to reduce μ. The weaker bonded ad-layers will be affected first and this indeed bears out the experimental results where second layers which initially form around the (112) or (011) planes are not permanent and appear to be redistributed over the surface. Thus the field increases the rate of migration of the adsorbed layer over the surface.

The field also reduces the activation energy[23] for the intense adsorption on the (001) area. The rate at which the area darkens as the work function rises, due to the increased surface potential, is increased by the influence of the field. The process however does not seem to occur at liquid nitrogen temperatures for the times of observation in these experiments although surface migration may be proceeding. Thus at higher temperatures material will have adsorbed on the (001) region and it is proposed that the sites initially filled will be those on the ridges where the ad-layer is relatively weakly held. The field then reduces the activation energy for the transfer from ridge to hole sites. Further migrating species will then fill the ridge sites so forming an intensely saturated monolayer. The two sites will have different energies of binding and so desorption would presumably occur first from the ridge sites and from the hole sites at higher temperatures.

Conclusions

The f.e.m. can give useful information on the problems associated with adsorption and catalysis. However care is needed when translating data obtained in this manner to "real" bulk surfaces. It has been shown that surface migration and the applied field can affect the ad-layer in quite a drastic manner. The doubts concerning the purity of the adsorbing gas and the nature of the desorbing gas will it is hoped be resolved in future work when an omegatron mass spectrometer is to be included in the system.

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Ion Bombardment of Metal Surfaces

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A review is presented of experimental work on physical processes occurring when noble gas ions of energy 0–10 keV strike metal surfaces with particular emphasis on sputtering, penetration and sorption. A simple theoretical expression is derived relating these latter three processes and is used to show that theoretical values of sputtering and penetration constants are in reasonable agreement with values obtained experimentally in work on sorption.

Introduction

Over a century ago, in 1858, Plucker[1] made the first recorded observations of ionic pumping when he noted a continuous reduction in pressure in a low pressure gaseous discharge tube when a current was passed through it. Only in the last 20 years however has work been done in an attempt to understand the physical mechanism of the phenomenon[2, 3] which has become very important with the advent of ion-getter pumps. The aim of this review is to discuss the possible reactions associated with noble gas ion bombardment of metal surfaces, in particular the penetration of 0–10 keV ions and sputtering of surfaces by them, and to relate the theoretical treatments of some of these reactions with experimental results taken in this and other laboratories. Only inert gas bombardments are considered since chemical processes between target and ion are numerous and may obscure the physical picture of the phenomenon.

Processes occurring as a result of ion bombardment

Under suitable bombardment and surface conditions energetic ions on reaching a metal target may (i) be reflected from the target surface, (ii) cause electrons or negative or positive ions to be emitted from the surface, (iii) liberate neutral particles from the surface (i.e. cause sputtering), or (iv) penetrate the target material and be trapped by it.

We shall briefly discuss the effects under headings (i) and (ii) before continuing with a more rigorous treatment of the phenomena of sputtering and penetration.

Reflection of positive ions

Positive ions incident on metal surfaces may be reflected without neutralization. A coefficient of reflection, R, is defined as the number of reflected ions per incident ion and several measurements of this coefficient have been carried out. Healea and Houtermans[4] bombarded nickel surfaces with noble gas ions and found that R increased with decrease in ion atomic weight. Values quoted for helium, neon and argon bombardment at 1 keV were : 0.56, 0.24 and 0.08, respectively, and are generally much higher than those obtained by other workers. For example Jackson[5] and Paetow and Walcher[6] have found reflection coefficients of the order of 0.02–0.03 for alkali ions striking various metal surfaces with energies up to 1 keV. Also Rostagni[7] has observed similar order coefficients for noble gas ions at a copper surface. Recently Hagstrum[8] has confirmed Rostagni's results using helium, neon and argon ions on clean tungsten and molybdenum surfaces. Reflection coefficients on tungsten were 0.0019, 0.0004 and 0.0001 for helium, neon and argon, respectively and were found to be essentially independent of the incident ion energy. Hagstrum's apparatus was able to determine the fraction of ions reflected as metastables and this fraction was found to be dependent on the incident ion energy. Hagstrum has suggested that the energy dependence of R found in earlier experiments may be due to the variation in the metastable component of the reflected particles.

It can be concluded therefore that reflection of ions occurs to a greater extent for lighter gases but the values are much lower than previously anticipated being less than 2 per cent on clean tungsten (Hagstrum). Although ions which are reflected do not contribute directly to target reactions, the processes occurring during reflection may transfer energy to target atoms which may then, in turn, cause sputtering[9]. This would be a factor for consideration in sputtering studies were R large.

Emission of charged particles due to ion bombardment

Electrons

Hagstrum has summarized the theories of ion neutralization and electron ejection up to 1953[10–12] and has produced strong experimental evidence that an Auger electron emission process takes place at energies below 2 keV. In Auger emission an electron from the conduction bands of the metal tunnels through the potential barrier to join the incoming

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ion, leaving the latter in an excited state. The energy liberated by the excited atom in reaching its ground state gives rise to the emission of another electron from the metal surface. This process is clearly governed by potential energy considerations, a fact which has been verified experimentally both by Hagstrum himself[13–15] for noble gas bombardment of tungsten and molybdenum surfaces at 10–1000 eV energy, and also by Bradley[16] who found that relative ejection coefficients from sodium by noble gas ions at energies of 0–2 keV were in the same order as the relative values of the potential energies of the ions.

Ionic emission

Honig[17] analysed the products of sputtering with a mass spectrometer when 300–400 eV xenon ions were striking a silver target and found that ions of both signs as well as neutral atoms of the target were liberated. He estimated that one positive ion was produced for every hundred striking the target. Bradley[18] extended Honig's work to the study of molybdenum, tantalum and platinum surfaces and observed that secondary ions of the base metals were produced under positive ion bombardment. Stanton[19] investigated the yield and energy distribution of these secondary ions from various metal surfaces when they were bombarded with ions of 1000 eV energy and found that the energy distribution of liberated ions was Maxwellian in form with a most probable energy of 10–20 eV.

Earlier work on negative ion emission[20–22] together with more recent studies[23, 24] indicates that the process occurs to only a small extent in the energy range considered (0.15–2 keV) and that most of the ions produced originate from adsorbed gases on the target surface rather than from the target material itself. Arnot and Milligan[20] estimated that only 0.64×10^{-3} negative mercury ions were produced per bombarding Hg^+ ion and 1.04×10^{-3} negative hydrogen ions for every H_2^+ ion at 200 eV ion energy.

Desorption of positive ions was noticed by Bills[25] when he heated tungsten, tantalum or molybdenum wire to 850°C after bombardment of the wire with low energy nitrogen ions or electrons. Riddoch and Leck[26] have carried out more detailed investigations of this phenomena using a mass spectrometer to determine the nature of the ions desorbed from a tungsten strip when it is heated after a period of bombardment by noble gas ions. They found that the desorbed ions were mainly potassium with some sodium and traces of rubidium and caesium and suggested that these alkali metals, present in the tungsten as impurities, were driven from the outer layers of the metal as ions. The ion bombardment was presumed to erode away the target surface, so exposing fresh quantities of the impurities According to Langmuir and Kindon[27] an atom adsorbed on a clean metal surface may lose a valence electron to one of the higher Fermi levels in the metal. In the case of the alkali impurities studied by Riddoch and Leck, the work function of the tungsten is greater than the ionization potential of the free impurity atom and these metals are consequently desorbed as ions. Bradley[18] has observed similar ionic desorption from a platinum target after bombardment with 1 keV inert gas ions.

Sputtering

Sputtering is defined as the removal of surface particles by positive ion bombardment. Observations of this phenomena were first recorded over a century ago by Grove[28] who noted the disintegration of cathodes in glow discharge tubes. Early experimental work to determine sputtering yields (atoms of bombarded material liberated per impinging ion) was also carried out in the glow discharge tubes where the ion beam was not monochromatic and pressures were too high. At these pressures the mean free path of liberated atoms is low and back diffusion of sputtered material to the target surface occurs to a considerable extent, thus reducing the effective sputtering rate. However work by Guntherschulze and Meyer[29], Penning and Moubis[30] and, later, by Fetz[31] was carried out at pressures low enough to make the back diffusion effect negligible ($p < 10\ \mu$). Penning and Moubis used a magnetic field to increase the electron path length so that their discharge could be maintained at lower pressures and Fetz employed a pool-type of cathode which enabled him to produce a high density ion beam at pressures of 1–2 μ. More recently Wehner[32] has used a modified form of Fetz's system, the target being inserted like a large Langmuir probe in the mercury vacuum-arc plasma. He has obtained results for mercury ion bombardment of twenty-six metals and has shown that the experimental conditions necessary for correct sputtering determinations are fulfilled. These conditions, laid down by Wehner himself[32] and also by Honig[17] are :

(i) The gas pressure must be low enough so that the mean free path of ions and sputtered atoms is large compared with the tube dimensions.

(ii) The ion current density must be high and the background pressure low so that formation of surface layers is prevented during sputtering.

(iii) The ions must strike the target normally, and

(iv) The discharge voltage drop should be low so that the formation of multiple charged ions is negligibly small.

In an attempt to reduce the pressure in the region of the target an ion beam method was developed by Seeliger and Sommermeyer[33]. This enabled them also to control the angle of incidence of the bombarding ions, a factor recently found to be important in sputtering measurements[34]. More recent work has been done using ion beams by Keywell[9] who drew out argon ions from a Philip's ion gauge cold cathode discharge and bombarded silver targets, by Gronlund and Moore[35], and by Burtt *et al.*[36] in these laboratories. Ion currents are generally lower than in the discharge method of Wehner but this is more than compensated for by the better vacuum conditions in the vicinity of the target. Also it is possible with this method to analyse the incident ion beam and therefore to cut out the effects of neutrals which can greatly effect sputtering measurements[37, 38].

Details of early experimental work on sputtering are given in a summarized review by Glockler and Lind[39] though this work must now be considered very much out of date. Massey and Burhop[40] have given a critical study of more recent work and Wehner[41] has also presented an excellent review on the subject up to 1955. Table I gives data for sputtering

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TABLE I

Sputtering coefficients for various gas–metal combinations

Ion energy (keV)	0.4	2	5	0.4	0.6	1	5	0.4	0.6	1	3	5	0.4	0.8	0.2	0.4	0.8	2	3	10
Ion	He	He	He	Ne	Ne	Ne	Ne	A	A	A	A	A	Kr	Xe	Hg	Hg	Hg	Hg	Hg	Hg
Tungsten				0.34[57]	0.32[57]				0.62[57]						0.3[88]	0.54[32]	1.3[88]	2.0[87]	2.75[87]	3.0[58]
Molybdenum				0.44[57]	0.54[57]				0.93[57]						0.1[32]	0.44[32]	1.0[88]	2.0[87]	2.75[87]	5.0[58]
Platinum					0.7[57]				1.56[57]						0.5[32]					10.0[58]
Aluminium				0.68[57]	0.83[57]				1.24[57]						0.14[32]	0.45[32]		1.5[87]		
Silver		0.36[35]	0.48[35]	1.6[57]	1.98[57]	2.3[29] / 2.4[9]	5.5[29] / 5.5[9]		3.4[57]	5.1[29] / 4.6[9]	7.0[9]	9.2[9]			0.85[88]					22.5[58]
Germanium	0.08[86]			0.63[86]	0.82[57]			0.92[86]	1.27[57]				0.91[86]	1.41[86]	0.21[86]	0.63[86]	1.23[86]			
Nickel					1.34[57]				1.52[57]						0.5[88]		1.4[88]		3.6[87]	7.0[58]
Iron				0.76[57]	0.97[57]				1.26[57]						0.13[32]	0.5[32]	1.1[88]	2.0[87]	2.75[87]	4.5[58]
Copper				1.53[57]											0.54[32]					12.0[58]
Gold				1.0[57]											1.0[32]			8.0[47]		21.0[58]

yields of various gas–metal combinations. It can be seen from it that there is still very little information in the energy range above 1 keV.

Several mechanisms have been suggested to explain the phenomena of sputtering. Among those now discarded is a theory proposed by Bush and Smith[42] which postulated that gas adsorbed by the target surface proceeded to expand causing a disruption of the target material. Also Thomson's proposal[43] that radiation is released as the ion strikes the surface and this in turn causes ejection of atoms of the target material has now been discarded. A mechanism which has survived is the " hot-spot " or, " thermal evaporation " process. This was proposed by von Hippel[44] in 1926 and suggests that the energy of the impinging ion is sufficient to raise the temperature of a small hemispherical region (of atomic dimensions) so that material is evaporated. This theory was developed further by Townes[45] to obtain an estimate of the absolute yield values and the calculation, applied to argon bombarding a barium target at low energy, was found to agree with an experimentally obtained result of Rockwood[46]. However this result has since been found to be too high.

The main criticism of the hot-spot theory has been that, at temperatures required to cause evaporation of the target, there should be considerable electron emission and this has not been observed. Also the velocities of the ejected atoms have been shown by Wehner[47] to be an order of magnitude larger than those of thermally evaporated atoms and the sputtering thresholds are greater than the atomic heats of sublimation.

Lamar and Compton[48] suggested that an ion may penetrate the target material, be reflected from a lower layer, and recoil to strike a surface atom in the outward direction. Modern theories are based on this mechanism but consider that many more internal collisions occur before final ejection of a sputtered atom. A typical modern theoretical approach has been given by Keywell[49] who suggested that the theory developed for the cooling of neutrons by collisions with the atoms of a moderator could be applied to sputtering. An incoming ion is presumed to penetrate the surface and strike a target atom. This atom is not itself sputtered, but in its turn collides with neighbouring atoms producing secondary displacements. The general effect on displaced atoms is similar to a diffusion process, or to a " random walk " of mobile atoms, and some of these reach the surface with sufficient energy to collide with and liberate surface atoms.

The final expression for the number of atoms sputtered per incident ion, S, using the above model is :

$$S = \left(\frac{\varepsilon E_o}{E_d}\right)^{\frac{1}{2}} \sum_{n=1}^{n_c} (F_p + 1.32\ \delta_{n1} F_r)\ e^{-\alpha\sqrt{n}} \cdot e^{-(n-1)\epsilon/2} \quad (1)$$

where $N_c = \dfrac{1}{\epsilon} \ln \left(\dfrac{\varepsilon E_o}{E_d}\right)$

$\delta_{n1} = 0\ (n \neq 1),\ = 1\ (n = 1)$

E_o = initial ion energy,

E_d = atomic displacement energy of target material,

ε = average fraction of energy transferred to target atom $= \dfrac{2M_1M_2}{(M_1 + M_2)^2}$ (M_1 = ion mass, M_2 = target mass),

F_p = probability of ion penetrating target,

F_r = probability of ion rebounding,

$\epsilon = 1 - \dfrac{(M_2 - M_1)^2}{2M_1M_2} \ln \dfrac{(M_1 + M_2)}{(M_1 - M_2)}$,

and α is a decay constant relating the number of atoms which escape from the surface n_e to the number of atoms displaced n_s, $\alpha = \ln \dfrac{n_s/n_e}{\sqrt{n}}$. When no atoms are sputtered $E_o = E_t$ and we have the relationship

$$E_t = \frac{E_d}{\varepsilon} \quad (1A)$$

ε may be evaluated, E_t can be found experimentally and therefore E_d, a constant hard to measure experimentally, is determined. This expression is shown by Keywell[9] to give a very satisfactory fit to experimental results.

Another theoretical treatment is given by Harrison[50–52] but this is very general and difficult to apply to actual cases because of the number of adjustable parameters it contains. Pease[53] has given a much simplified mean free path theory leading to the following sputtering formula :

$$S = \frac{\bar{E}}{4E_d} \left[1 + \left\{\frac{\ln \bar{E}/E_s}{\ln 2}\right\}^{\frac{1}{2}}\right] \sigma_p \cdot n^{2/3} \quad (2)$$

where $\bar{E}$ = average energy transferred from an ion to a target atom, E_d = displacement energy, E_s = energy required to remove an atom from the target surface, n = number of atoms per unit volume, and σp is the displacement cross section in collision. Values calculated from this expression by Gronlund and Moore[35] show that they are consistently about one half those measured experimentally, indicating that the picture provided by the collision theory is essentially correct.

Several workers have found the relation $S \propto \ln E/E_t$ to hold for sputtering. Goldman and Simon[54] quote

$$S = \frac{M_1}{M_2} \ln \left(\frac{E}{E_t}\right) \sec \psi$$

for bombardments at incident angle ψ above 50 keV, and Strachan and Harris[55] have found $S = 2 \ln E/Et$ for 0.1–20 keV Hg^+ and A^+ ions sputtering carbon and ion targets. Pleshivtsev[56] has also found that the sputtering rate varies with $\ln E/E_t$ for 15–50 keV H_2^+ ions striking a copper target. It should be mentioned in passing that his data also indicates that, at intermediate ion energies, a process involving momentum exchange is of greatest importance in the sputtering mechanism.

The value of the sputtering coefficient has been found to vary considerably with the nature of the ion and target material considered as is evident from the above formulae. However it has been found in general that S increases with ion mass, though exceptions do occur with chemically active gases. For example mercury bombardment of surfaces

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which form an amalgam produces much higher yields than those obtained by bombardment of non-amalgamating materials.

At first sight the variation of S with the atomic number of the target material appears to be quite erratic[32]. However it has recently been shown by Laegreid *et al.*[57], Wehner *et al.*[58] and Henschke[59] that the sputtering yield depends on the condition of the " d " shells of the atoms of the target material. Progressing through the periodic table S is shown to pass through maxima for targets with atoms having the " d " shells filled up.

The effect of varying the angle of incidence of the ions on the sputtering yield has been demonstrated by Fetz[31] who observed the yield for molybdenum wires of varying diameter. For thinner wires, where a large percentage of the ions struck obliquely, the sputtering yield was much larger than for large diameter targets where results approximated to those obtained for normal incidence. More information on this effect has been presented by Wehner[34] who studied the change in shape of spherical targets when bombarded by a unidirectional beam of mercury ions. The spheres presented continuously varying angles to such a beam and altered shape due to preferential sputtering at certain incident angles. Eventually a conical surface remained and this receded unchanged under further ion bombardment. Materials investigated were found to form three distinct groups : those exhibiting only slight changes in S with incident angle (gold, silver, copper and platinum), targets with intermediate responses (nickel and tungsten), and metals for which the sputtering yield was greatly influenced by the incident angle (iron, tantalum and molybdenum).

Penetration of ions into metals

A knowledge of the penetration depth and energy loss of ions is basic in the understanding of processes occurring due to the interaction of these particles with matter. It is surprising therefore to find that very little work has been done in this field in the ion energy range of 0–20 keV. Young[60], studying the penetration of 0–11 keV light ions into aluminized phosphors, has found that the relation $R = k.E^{0.83}$ holds, where R is the range in nicroms, E is the ion energy in keV, and k is a constant with values 0.2 for H^+ and He^+ ions and 0.15 for H_2^+. In earlier work Young[61] bombarded ZnS:Ag phosphors with H^+, H_2^+, He^+, Ne^+, N_2^+ and A^+ ions at energies of 1–25 keV and found generally that an approximately linear relationship between the penetration depth and the energy holds. (We have assumed such a relationship to hold in compiling Table II, where penetration depths obtained by various workers over a wide range of energies have all been normalized to 1 keV for comparison).

A useful technique for studying penetration of ions is one involving radioactive tracers. The experiment comprises bombardment of the surfaces with radioactive gas ions followed by a removal of the surface in stages. By measuring

TABLE II

Penetration depths normalized to 1 keV for various gas–metal combinations

Investigator(s)	Bombarding ion	Target Material	Energy used (keV)	Depth/keV (Å units)
Koch[76]	Ne	Silver	60	1.7
Young[60]	H or H_2	Aluminium	1–25	200
	He	Aluminium	1–25	150
				80
	H			40
	H_2			90
Young[61]	He	ZnS:Ag powder	20	50
	Ne	Phosphor		25
	N_2			25
	A			
Bredov and Okuneva[62]	$Ce^{134} + Ce$	Germanium	4	250
Bartholomew and La Padula[63]	Kr^{85}	Nickel	0.15	51,000
Reynolds and Zucker[89]	N_2	Ilford C-2 Emulsion Film	20,000	6.5
Gillam[70]	He	Cu_3Au alloy	4	10
	A			10
	Xe			10
Burtt *et al.*[36]	A	Tungsten	2	25
Davies *et al.*[64]	Rb^{86}	Aluminium	30	37
	Na^{24}			61.7
	Cs^{137}			61.7
Hines and Arndt[90]	H_2	Quartz	5–60	117
	He			121
	Ne			19
	A			18
	Kr			15
Belyakova and Mittsev[91]	Li	Aluminium	1–2	10
Colligon and Leck[84]	A	Molybdenum		4.1
		Tungsten	1.7	5.0
		Platinum		3.2
Nielsen[68] (Theoretical)	A	Tungsten	1	4.75
Gianola[92]	He	Single crystal Silicon	30	300

the residual activity of the target at each stage of erosion the depth distribution and maximum depth of penetration of the embedded ions can be determined. Work on these lines has been done by Bredov and Okuneva[62] using 4 keV caesium 134 ions on germanium, Bartholomew and La Padula[63], who bombarded nickel targets with 150 kV Kr^{85} ions, and Davies *et al.*[64, 65], who have bombarded aluminium targets with 2–50 keV radioactive alkali metal ions. In a later publication Bredov *et al.*[66] presented a theoretical treatment on the penetration of germanium by caesium and were able to show that their results were of the right order of magnitude. Penetration values obtained by Bartholomew and La Padula are not in line with theoretical treatments however being much too high for the low bombarding energies employed.

A general theoretical treatment of the penetration of atomic particles through matter has been presented by Bohr[67]. He shows that the many-bodied problem involved in slowing down a particle can be simplified by considering two distinct types of collision process : electronic (inelastic) collisions, causing ionization or atomic excitation, and nuclear (elastic) collisions. Nuclear collisions are more significant when particle velocities are less than 2×10^{-8} cm/sec, the slowest orbital velocity of electrons in the stopping material. Bohr's expression for the range of fast particles in solids has been used by Nielsen[68] who found good agreement with his experimental results. Also Davies and Sims[65] have found that the Bohr–Nielsen expressions give the right order of magnitude for the penetration depth of alkali metal ions in aluminium. They point out however that, although theoretical penetration depths increase with increasing ion–target mass ratio, as observed experimentally, the theoretical change is too large. It will be interesting to see whether further work on penetration confirms this shortcoming of the Bohr–Nielsen expression.

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According to Nielsen[68] if the mass of the incident ion (M_1) is greater than that of the stopping material (M_2) the ion penetrates with little oscillation about its direct line of flight. If $M_1 < M_2$ however a random walk process occurs which can be represented by equations governing neutron diffusion[69]. Expressions derived by Nielsen for the range in the above-mentioned cases are :

$$M_1 > M_2 \quad \frac{R}{E} = \frac{0.6}{100\varrho} \cdot \frac{M_1+M_2}{M_1} \cdot M_2 \cdot \frac{(Z_1^{2/3}+Z_2^{2/3})^{1/2}}{Z_1 Z_2} \quad (3A)$$

$$M_1 < M_2 \quad \frac{R}{E} = \frac{0.7}{100\varrho} \cdot \frac{M_2^2}{M_1+M_2} \cdot Q \cdot \frac{(Z_1^{2/3}+Z_2^{2/3})^{1/2}}{Z_1 Z_2} \quad (3B)$$

where R is the range in microns and E the ion energy in keV. Z_1 and Z_2 are the atomic numbers of the ion and target material respectively, ϱ is the density of the target material and

$$Q = [\varepsilon(1-\overline{\cos\theta})]^{-1/2}$$

where $\overline{\cos\theta}$ = the average cosine of the scattering angle per collision in the laboratory system and ε = the average logarithmic energy decrement per collision. Gillam[70] has shown that Q may also be written :

$$Q = \left\{\left[1+\frac{(M_2-M_1)^2}{2M_1M_2} \ln\left(\frac{M_2-M_1}{M_2+M_1}\right)\right]\left[1-\frac{2M_1}{3M_2}\right]\right\}.$$

For bombardment conditions where $M_1 \simeq M_2$ Nielsen's treatment does not hold as the impinging particles may lose all their energy in a single collision. An expression to cover this region has however been derived by Davies and Sims[65] who quote an expression of the form :

$$\frac{R}{E} = k\ 1.12\ \frac{M_2^2}{M_1+M_2} \cdot \frac{(Z_1^{2/3}+Z_2^{2/3})^{1/2}}{Z_1 Z_2}$$

where k is a function of the mass-ratio and is derived from theoretical distribution plots obtained by the Monte-Carlo method.

Sorption of ions

Pietsch[71] has reviewed earlier research on gas clean-up up to 1926 and it is clear from his article that several clean-up mechanisms exist. The first, known as " chemical clean-up ", was found to depend on the presence of some chemical reagent which removed the gas molecules as a result of their interaction and formed stable compounds. Malignani[72], in 1894, made use of this technique for removing residual gases from a carbon filament lamp. The absorptive media used in his experiment was a viscous suspension of red phosphorous and this would now be referred to as a " getter " since it receives and holds gas.

A second process, designated by Langmuir[73] as " electro-chemical ", occurs only when an electronic discharge is operating but relies on a chemical reaction to remove the gas. The effect of ionization in this case is to direct the ions towards surfaces at which they react and to hold them there for a longer time than the atoms would normally settle on the interface, thus increasing the time available for the reaction to take place.

Finally, when the disappearance of the gas cannot be accounted for by any chemical processes, as is the case with rare gases, ionic pumping where ions penetrate into and are trapped by a suitable collector held at a negative potential is the sole mechanism responsible. Langmuir has designated this mode of pumping as electrical or " electro-mechanical ".

We will limit this article to a discussion of the latter pumping mechanism. Dushman[74] has published an excellent review of the general phenomena of ion pumping and Carter[75] has discussed fully the early experimental work carried out in this field. In the last decade considerable work has been done on sorption using various gas–metal combinations and it is generally found that, for a particular ion energy a saturation value in the number of ions sorbed is quickly reached.

In 1948 Koch[76] bombarded silver, aluminium and tungsten discs with 60 keV neon ions. Almost complete release of the neon resulted from heating *in vacuo* and a saturation value was reached when about 6×10^{16} ions/cm^2 had struck the targets. Reddan and Rouse[77] bombarded both oxide coated nickel mesh cathodes and tantalum probes with helium ions and found evidence of considerable clean-up, not reaching saturation. Not all the helium was re-liberated, even on heating the bombarded materials to 2000°C where, at best, 70 per cent of the sorbed gas was recovered.

Brown and Leck[78] studied sorption of He, Ne, A, Kr, N_2

and O_2 ions by nickel, molybdenum and aluminium electrodes in a Penning gauge. Instead of heating the electrodes after the primary ion bombardment, however, they proceeded to bombard them with ions of a second gas. Sputtering of the surface by the second gas uncovered and liberated buried ions of the first gas and total quantities of gas recovered in this manner were comparable with those obtained by heating the target. Saturation sorption levels were observed in all cases except for helium bombardment and there was no evidence of sorption without the presence of the discharge.

Whilst undertaking studies on bombardment cleaning of titanium and germanium Farnsworth *et al.*[79] and Dillon and Farnsworth[80] noticed larger rises in pressure during the annealing cycles than are observed when the targets are annealed without the preceding bombardment. This effect was most probably due to the presence of argon sorbed by the germanium and titanium surfaces during the discharge period.

Varnerin and Carmichael[3] have studied the pumping of helium by molybdenum surfaces at energies of 0.15–2.6 keV using a tube in the form of a coaxial tetrode where the outer can is the molybdenum collector. They found that a saturation value for the number of ions pumped was reached and attempted to explain this saturation on the basis of a re-emission phenomena. Von Meyern[81] and Young[82] had already suggested a re-emission mechanism where the rate of release was dependent solely on the amount of gas trapped. However Varnerin and Carmichael's work indicated that this rate was also dependent on the time at which the trapping had occurred, as if the ions had penetrated the target surface and were again released after a short time. In later work Carmichael and Trendelenburg[83] further attempted to explain this re-emission mechanism on the basis of a penetration of ions coupled with an erosion of the surface due to sputtering. This suggestion would mean that ions previously buried in the target would effectively approach the surface during the erosion where they are released into the gaseous phase. They further proposed that, after some time, the number of ions released will be equal to the number sorbed so that a saturation is reached. Since both penetration of ions and sputtering of surfaces by them are now well known phenomena, as can be seen from the preceding two sections, the explanation given by Carmichael and Trendelenburg is very satisfactory. Work in these laboratories[36,84] can also be explained on the basis of a penetration function which moves with the sputtered surface, and the value of the maximum depth penetration of the ions required to fit the theoretical to the experimentally obtained results is comparable to that obtained by other workers (see Table II). Fig. 1 shows the agreement between the theoretical and practical build-up curves for argon ions striking a tungsten target at 1 keV.

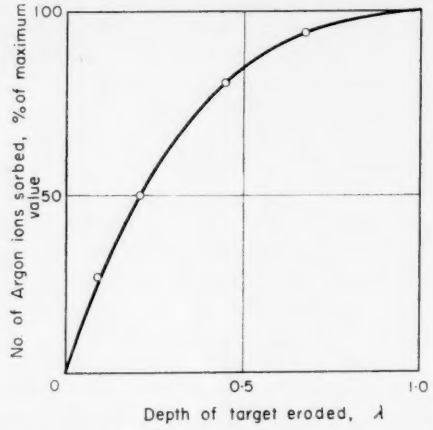

FIG. 1. Comparison of theoretical and experimental sorption curves for argon ions bombarding a tungsten surface with 1 keV energy. ○, Experimental values ; ——, Calculated curve.

Blodgett and Vanderslice[38] have also proposed that re-liberation of ions by sputtering is the cause of the observed saturation level in the quantity of gas cleaned up. The main part of their work, however, was carried out under entirely different conditions where sputtered deposits continually landed on the ion collector during bombardment so burying the sorbed ions. Hence they observed no saturation, even after over 100 equivalent monolayers of gas had been cleaned up.

To conclude this section we have evaluated, where possible, the saturation values obtained by various workers of the number of ions sorbed on various collector materials (Tabie III). Work in this laboratory[36, 84] has indicated that this

TABLE III

Number of ions sorbed/cm²/keV energy

		Helium	Neon	Argon	Krypton	Actual voltage (keV)	Ion bombardment
Uranium	(93)				0.72×10^{13}	40	8×10^{17} ions
Germanium	(94)			1.00×10^{15}		0.4	2×10^{16}
Nickel	(83)		6.23×10^{15}	3.56×10^{14}	6.22×10^{13}	0.10	4.45×10^{15}
	(95)				6.12×10^{13}	0.18	4.5×10^{15}
Molybdenum	(3)	1.71×10^{17}				1.1	2×10^{17}
Tungsten	(78)	1.7×10^{16}	6.7×10^{15}	3.8×10^{15}	2.8×10^{14}	2	3×10^{16}
Tungsten	(36)		7.2×10^{15}	1.6×10^{15}	6.3×10^{14}	1	4×10^{16}
Molybdenum	(84)		1.5×10^{16}	3.0×10^{15}	1.8×10^{15}	1	2×10^{17}
Platinum	(84)			3.5×10^{15}	1.0×10^{15}	1	3×10^{17}
Silver	(76)		5×10^{14}			60	6×10^{16}

saturation level is proportional to the ion energy in the region 300–3000 eV. We have therefore normalized all the results to a common bombardment energy of 1 keV for comparison.

Conclusions

It is clear from the preceding discussion and from Tables I and II that, in the energy range considered (0–10 keV) ions cause sputtering and at the same time penetrate metals. Also Table III indicates that some of the penetrating ions are sorbed. The number of ions sorbed by a given target is seen to reach a maximum saturation value and this indicates that a stage is reached where either no more ions are sorbed or the extra number sorbed is always equal to the number released. The explanation of Carmichael and Trendelenburg[83] mentioned in the previous section considers the second of these possibilities. They postulate that the probability of sorption of ions is such that the number uncovered and released by the sputtering process in any given time is equal to the extra number sorbed. It has been shown by Burtt *et al.*[36] that using this model and a probability function which falls off linearly from a maximum value at the target surface to zero at some depth λ_{max} (the maximum possible penetration depth of the ions) a saturation level is reached when a depth λ_{max} of the target material has been sputtered away. Thus, if S is the sputtering rate, Ni_S the number of ions per unit area required to cause saturation, and U the atomic density of the target material :

$$Ni_S \times S = \lambda_{max} \times U. \qquad (4)$$

This equation is most useful as it relates the three ion bombardment processes discussed in detail in this review. It must be emphasized however that the treatment used to derive equation (4) uses the simplifying assumptions that the probability of sorption is independent of the number of ions already sorbed by the target, that diffusion effects are negligible, that the bombardment and sputtering rates are constant and uniform over the target surface, and that all the ions previously sorbed and subsequently exposed by sputtering are re-liberated into the gaseous phase. Later treatments have shown that, using the same simplifying assumptions, equation (4) holds for any probability function $\varrho(x)$ where x is the depth from the target surface and $\varrho(x) = 0$ at $x = \lambda$.[78]

It is difficult at the present time to show whether equation (4) is justified or not owing to the uncertainty in both the sputtering data and the penetration values. A theoretical treatment of the penetration depth using Nielsen's formula yields the most probable depth, not the maximum which may be ten times higher (see Table II). Also the formulae for sputtering derived by Pease (equation 2) does not give accurate values in this region. Table IV presents values obtained theoretically by Pease for 1 keV argon striking molybdenum, tungsten and platinum surfaces compared with values extrapolated from Laegreid and Wehner's[57] results and illustrates that, although the order of magnitude is correct results are not reliable. Only a general agreement can therefore be expected for equation (4) with so many uncertain parameters. Assuming that the maximum penetration depth is, in fact, ten times the value obtained from Nielsen's formula equation (4) may be re-written in the form :

TABLE IV

Comparison of sputtering coefficients determined theoretically and experimentally

	Molybdenum	Tungsten	Platinum
Theoretical value (Pease[53])	1.5	1.5	1.1
Experimental value (Extrapolated from Laegreid and Wehner's curves[57])	1.0	0.6	2.0

$$\frac{10\lambda}{S} = \frac{Ni_S}{U}. \qquad (5)$$

The quantity Ni_S has been measured in this laboratory for neon, argon and krypton striking tungsten and U the atomic density is, for tungsten, 6.2×10^{22} atoms/cm^3. Thus the right hand side of equation (5) is known fairly accurately and can be plotted as a function of the ion-target mass ratio (Fig. 2). The left hand side of the equation has been computed by using Nielsen's formula for λ and by extrapolating Wehner's sputtering results. This has also been plotted in Fig. 2 for comparison. Bearing in mind the approximations used for the $10\lambda/S$ term the agreement between the two curves is very satisfactory.

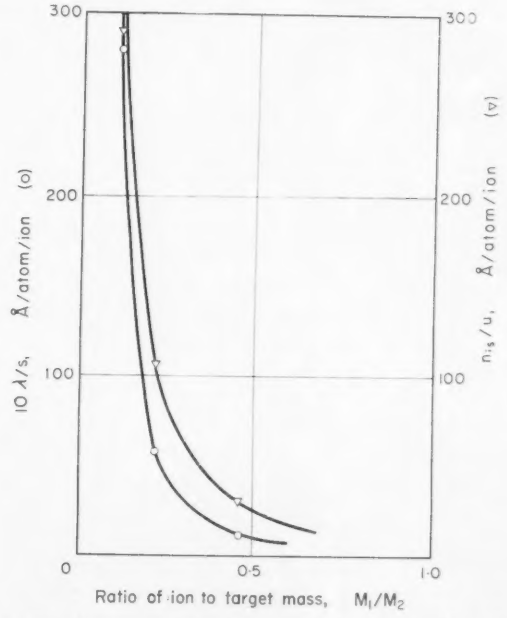

FIG. 2. Showing the variation in the two sides of equation (5) with the ion–target mass ratio for various gases striking a tungsten surface ($M_2 = 184$).

At the present time sputtering theories are still in an elementary stage. The statistical approach of Harrison was mentioned only briefly in the text as it is particularly complicated and not yet complete (certain parameters have still

to be identified). This theory does however consider the sputtering process in detail and is worth further mention here. Ions are presumed to penetrate several atomic layers before making their first collision. In these collisions they transfer some of their energy to, so called, " primary " knock-on target atoms which, in turn, agitate secondary and tertiary atoms. Each of the above-mentioned groups (ions, primary knock-on atoms, etc.) is treated individually and all the particles are shown to contribute to a general thermal equilibrium several atomic layers below the target surface. Out of this disturbed region atoms are eventually ejected in the surface direction. However they are now moving much slower than the incident ions and cannot traverse the same number of atomic layers back to the surface, in fact they rarely travel more than one atomic layer. Consequently the probability of a disturbed atom striking a surface atom with sufficient energy to sputter it is extremely small and this fact, at first sight, raises some doubts about the validity of the theory. This problem is eliminated however if the concept of a " chain mechanism " is introduced[96]. In single crystal targets there are generally close-packed lines of atoms terminating on the surface. If the internal ends of these chains are struck shock waves pass through them liberating the surface atoms without moving the intervening particles. The process is analogous to that occurring when a line of billiard balls is struck by a further ball, only the last ball in the line is propelled away. Thus, although the disturbed " tertiary " and lower order " knock-on " target atoms cannot themselves reach the surface, they may, by the chain mechanism described above, induce surface atoms to be sputtered. An interesting fact resulting from this consideration is that the sputtered particles will tend to leave in preferred directions (i.e. along the lines of the chains), a fact observed experimentally in single crystal work[97]. In polycrystalline targets the chain mechanism still applies but now of course there is no preferred direction for the sputtered particles. The success of this theory can be shown by the agreement between theoretical and experimental results[52]. The final expression still contains two adjustable parameters and is difficult to apply to actual cases. Also it must be emphasized that the theory is " statistical " dealing with average effects so that localized sputtering phenomena, such as the development of spot patterns on a sputtered surface, cannot be accounted for.

In conclusion it can be stated that reflection of ions, ion-induced electron and ionic emission, sputtering, penetration and sorption can occur in the 0–10 keV energy region when ions strike metal surfaces. Ion reflection and ionic emission are minor processes, the latter occurring due to the presence of alkali metal impurities in the target material or adsorbed impurity layers on the surface of the target. Electron emission is critically dependent on the cleanliness of the surface of the material investigated and depends on the transference of the potential energy of the incoming ion to provide the energy necessary for an electron to be ejected. Sputtering occurs to varying extents for different ion–metal combinations generally increasing with ion mass and being larger for targets where the electronic " d " shells are full. A reasonable figure for the sputtering yield is given by a formula derived by Pease[53]. Satisfactory values of the penetration depth can be derived from the expression quoted by Nielsen (equation 3). The depth is found to be linearly dependent on the energy of the incoming ion. Finally, work on sorption shows that as the bombardment proceeds more ions stick to the target up to a saturation level. After this saturation condition has been reached it is proposed that the extra number of ions sorbed by the target is equal to the number re-liberated by sputtering. This assumption is tested by plotting equation (4) and reasonable agreement is obtained. Equation (4) is interesting as it relates the number of ions required to load a target to saturation to both the penetration depth and the sputtering coefficient and it is hoped that further work may help to confirm this relationship.

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Observations of Crystal Orientation Effects in Tin-Telluride Thin Films

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Tin-telluride thin films may be crystallographically oriented to certain preferred directions either during evaporation on to glass substrates or during subsequent anneals. X-ray diffraction measurements reveal the effects of ambient gas and ambient gas pressure, and annealing ambient. Either {110} or {111} planes show preferred orientation when helium is used as evaporant ambient, while {100} planes show preferred orientation in argon. Annealing in vacuum produces {111} orientation while annealing in tellurium vapor produces {110} orientation. Crystallite size measurements reveal preferences related to growth of larger crystallites of preferred crystal direction normal to substrate as compared to unpreferred crystallites during evaporations of films. Size measurements indicate regrowth of preferred crystallites larger in plane of film during annealing. Two mechanisms are suggested to explain orientation effects in evaporation ; scattering of evaporant atoms by the ambient gas and adsorption/occlusion of ambient gas into the film. The inclusion of tellurium in regrowth is suggested as an explanation of the different regrowth habits in vacuum and tellurium vapor.

Introduction

Orientation of thin films on crystal substrates has been a subject of interest, as described in the recent paper by D. A. Brine and R. A. Young of the Engineering Experiment Station, Georgia Institute of Technology[1]. Relatively few observations have been made of orientations of thin films on amorphous substrates[2–5]. While the mechanisms involved in such orientations are not known, it is of interest to study the effects of various parameters of the system used to lay down the films.

Tin-telluride has been of interest recently for its possible use as a carrier alloy in contacts to intermetallic semiconductors. The application of such contacts as thin films has proven a useful method of device fabrication for high frequency applications. It was in the course of such investigations that film orientations was first observed. Effects of the pressure of two ambient gases, helium and argon, upon the film orientation and the effects of annealment in vacuum or in tellurium vapor have been studied.

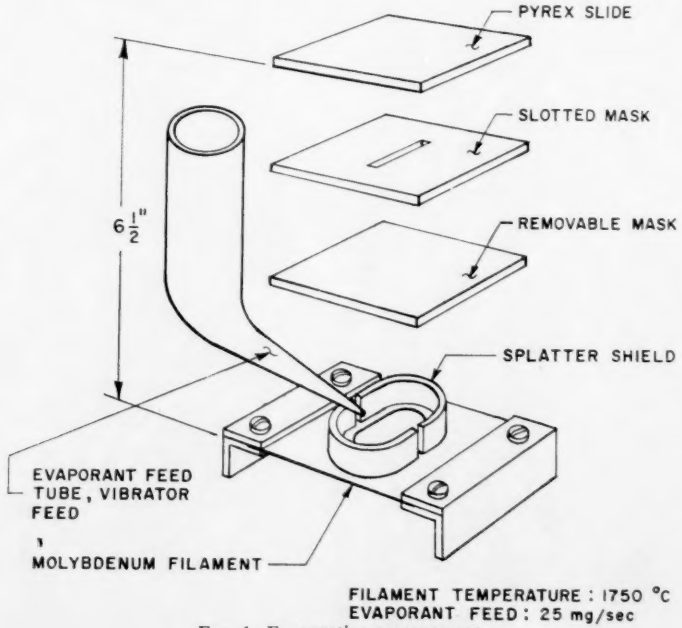

FIG. 1. Evaporation arrangement.

Evaporation procedure

Pyrex glass slides were thoroughly cleaned in acid and washed in "ion-exchange" water before being placed in the evaporator. They were further cleaned by ion bombardment during pump down. The tin-telluride was prepared fresh and powdered under liquid nitrogen just before being placed in the evaporator.

The vacuum system was first pumped to 1×10^{-6} Torr by a diffusion pump whereupon a Meissner trap was employed to condense most of the remaining vapors out of the system atmosphere. The resulting pressure was about 1×10^{-7} Torr. Helium or argon, dried by a passage through a molecular sieve and cleansed of oxygen by passage through Deoxo was bled into the vacuum chamber by a controlled leak. The pressure was measured by a Kinney ionization gauge and was controlled within $\pm 1 \times 10^{-5}$ Torr of the desired pressure during evaporations. Some of the increased pressure was undoubtedly due to scattered tin and tellurium so that the actual ambient gas pressure was lowered during evaporation. The ambient gas pressure was not independently measured.

Because tellurium is a gas at the temperatures necessary to evaporate tin-telluride, a flash evaporation technique was employed. The powdered evaporant was fed (Fig. 1) from a constricted shaker tube on to a hot molybdenum ribbon. The ribbon was maintained at such a temperature that the evaporant powder particles vaporized without wetting the filament. The slotted mask could be moved laterally, allowing evaporations at several different ambient pressures to be laid down on the same glass slide. Films were evaporated on four slides in separate runs for each ambient gas used.

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Measurement of film orientation

A Norelco X-ray diffractometer was used for the orientation measurements. Copper K_α radiation was employed, and detected by a Norelco Proportional Counter. Pulse height discrimination was used together with enough Nickel foil filters that the K_β diffractions were not discernible above background. The PHD effectively blocked out high energy background and harmonic wavelength diffraction contributions.

A diffraction stage attachment was constructed which allowed the glass slides to be traversed in the plane of the film under the incident X-ray beam. Measurements could then be made on the several films applied to each glass slide. The traverse arrangement also allowed each film to be examined for variation in orientation. A slide could also be cut, rotated 90°, and examined for orientation variation. This was necessary since the diffractometer employed a line configuration incident beam. The diffraction technique just described observed only those crystallites in the film which were oriented with particular {hkl} planes parallel to the glass substrate. The diffractometer rate meter recorder traces thus measured the number of the crystallites of each orientation observed.

It must be remarked that several other factors beside the number of oriented crystallites also affect diffraction peak height. The structure factor of each reflection and the multiplicity of the {hkl} planes, making up the symmetry associated set of {hkl} planes, influence the intensity of each different {hkl} intensity measured. However, these factors are constant for each {hkl} reflection. Crystallite size and inhomogeneous strain line broadening may also affect peak intensity. Increased crystallite size would reduce the observed line halfwidth and increase peak intensity. Part of the effects observed was due to changes in crystallite size as will be shown. Since all films were evaporated in reasonably equivalent conditions, other than ambient pressure or annealment ambient gas, strain line broadening effect upon changes in line peak intensity was assumed negligible.

Two complete scans were run on each film with the beam incident on different areas of the film and the traces compared for reproducibility. Peak intensities varied less than 5 per cent among traces indicating only slight variations in orientation throughout each film. Occasional checks on intensities measured with films rotated 90° confirmed this uniformity.

Line halfwidths were measured with the same diffraction equipment. Instrument broadening was determined by measuring halfwidth with successively smaller beam split systems. The measurements were then extrapolated to zero beam width. Jones's[6] corrections were applied for $K\alpha$ doublet broadening. Ekstein and Siegel's[7] corrections were applied for spectral broadening. The corrected halfwidths were then used in the Scherrer[8, 9] equation to calculate crystallite sizes. Values obtained are estimated to be accurate to within ±5 per cent.

Effects of ambient pressure

When helium was used as the ambient atmosphere during deposition the resulting films exhibited two preferred orientations (Fig. 2). At a pressure of 5×10^{-5} Torr a strong {111} orientation was observed while at 1×10^{-3} Torr a {110} preference occurred. It must be remarked that in Fig. 2, and the subsequent figures of diffraction traces, the traces measured of different films are offset in the ordinate (intensity) direction for clarity of presentation.

When argon was used as the ambient atmosphere, a strong {100} preferred orientation (Fig. 3) occurred when the film was deposited at 1×10^{-4} Torr.

Crystallite size determinations (Table I) (by diffraction line halfwidth measurements) were made for the three orientations of crystallites measured. These values indicate the average thickness of each type of crystallite normal to the film surface.

TABLE I

Crystallite sizes ($\times 10^{-8}$ cm)

Crystal orientation	Argon pressure (Torr)		
	1×10^{-5}	1×10^{-4}	1×10^{-3}
{100}	950	1000	650
{110}	570	270	370
{111}	580	220	230

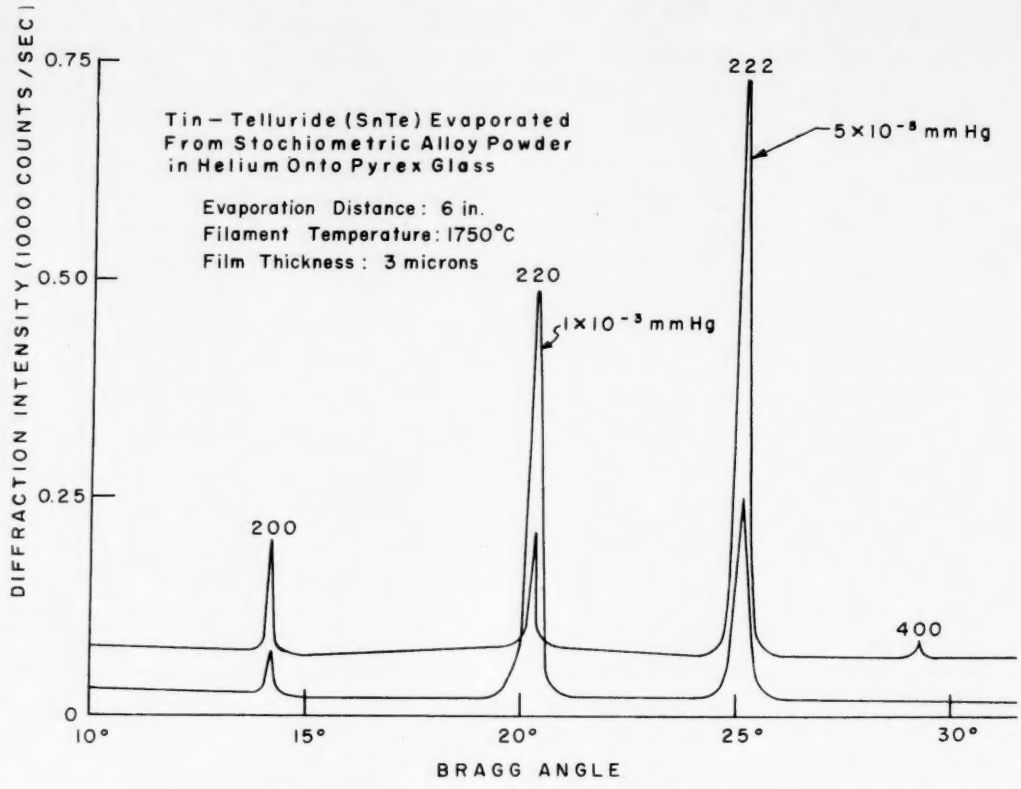

FIG. 2. Effect of evaporation in helium ambient.

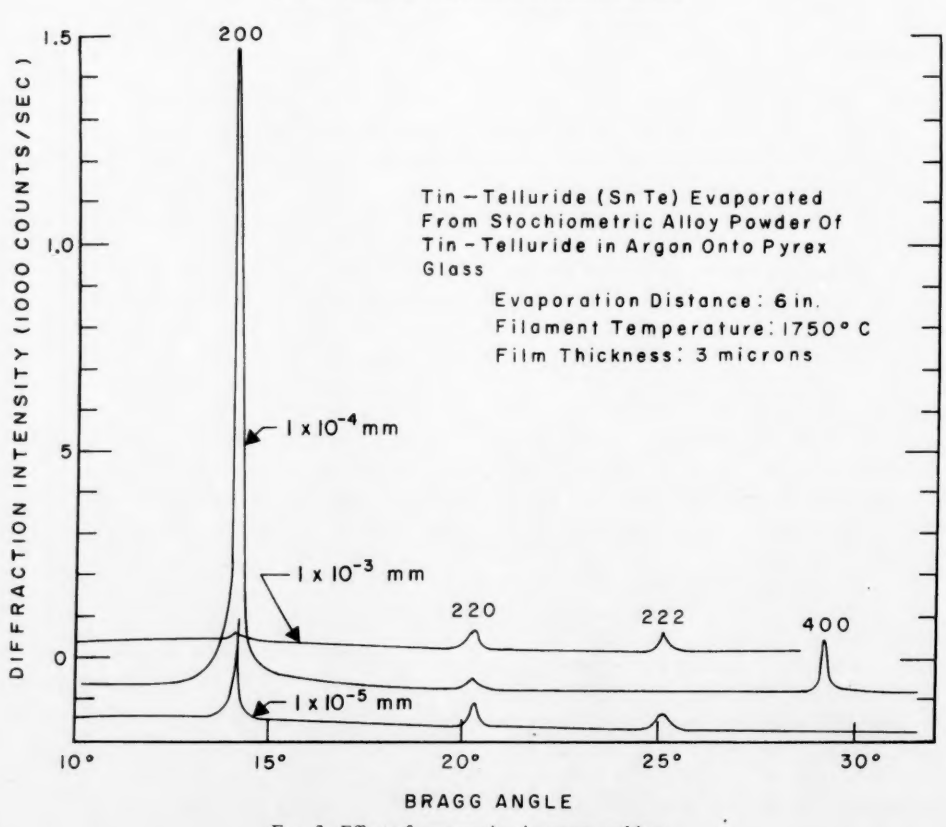

FIG. 3. Effect of evaporation in argon ambient.

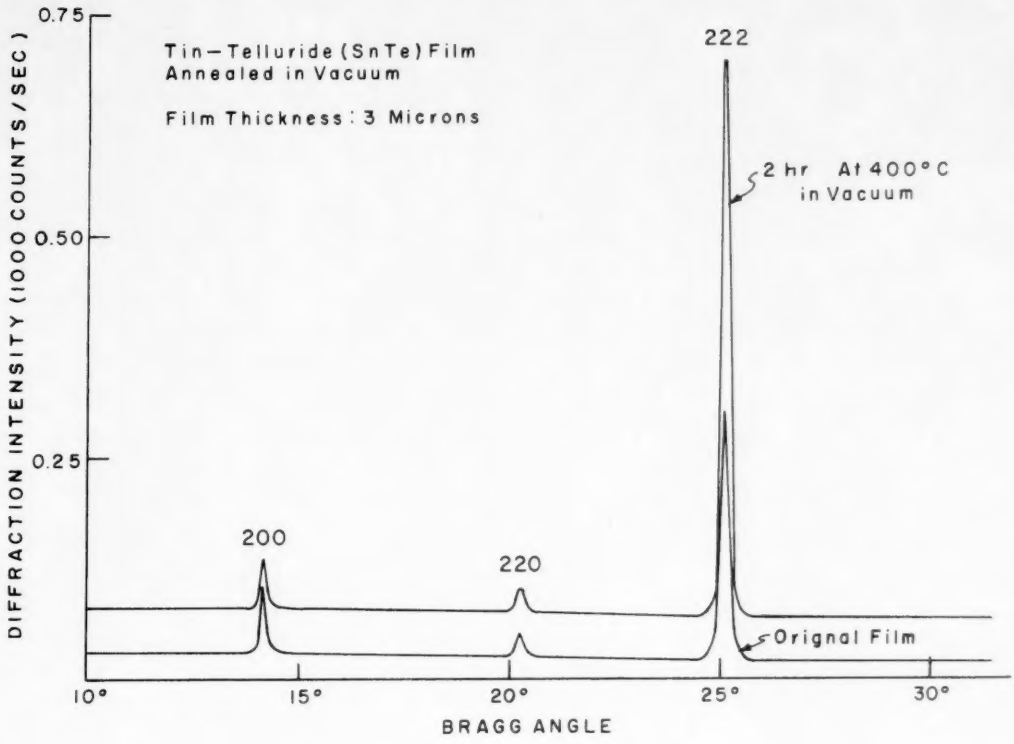

FIG. 4. Effect of vacuum anneal.

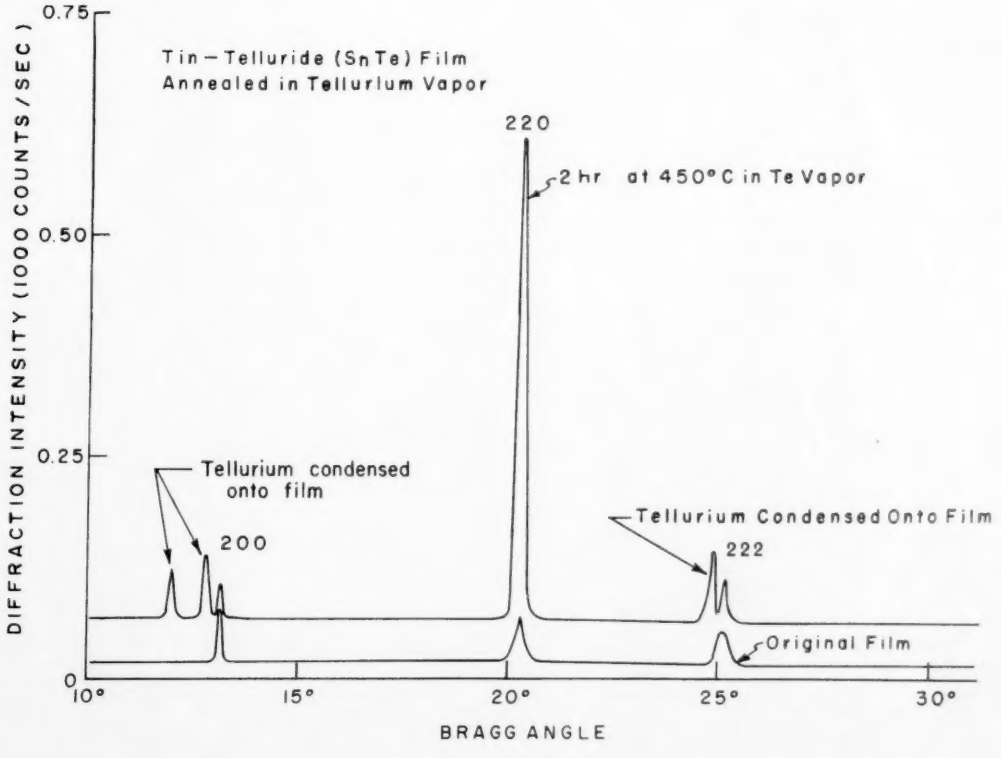

FIG. 5. Effect of anneal in tellurium vapor.

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Effects of annealment atmosphere

Three films each were annealed in vacuum and in tellurium vapor. Quartz ampoules were prepared and flamed out under vacuum. The films on the pyrex slides were then sealed in the ampoules under vacuum. If tellurium vapor was desired during annealment, enough tellurium was added at one end of the ampoule to maintain the necessary vapor pressure at the annealment temperature. The ampoules were then placed in an inconel tube inside a furnace for annealment. Samples were annealed at 400 °C in vacuum for periods of 2–52 hr and at 450 °C in tellurium vapor (0.15 Torr) for 2 hr. Annealed in vacuum the films tend to orient with the {111} parallel to the substrate (Fig. 4). Annealed in tellurium vapor the films tend to orient with the {110} parallel to the substrate (Fig. 5).

The crystallites grow during the annealing such that after annealment all crystal orientations normal to the substrate exhibit crystallite dimensions of 1100–1300 $\times$ 10^{-8} cm thickness.

Discussion

Effects of ambient pressure in film orientation

The observed orientations of the films in helium and argon suggest two possible mechanisms influencing crystallite growth, a scattering of evaporant by the ambient gas and an adsorption of ambient gas onto the substrate or occlusion into the film. The scattering mechanism is suggested in the variation of orientation with pressure. In argon at 1×10^{-5} mm the film resembles a true powder in that its diffraction trace correlates with the powder diffraction data as published by A.S.T.M. Also the crystallite sizes (Table I) suggest a reasonably uniform crystallite distribution. At 1×10^{-3} mm, however, the film exhibits all diffractions at low intensities and the crystallite size is considerably reduced, suggesting scattering of evaporant atoms. Film orientation effects are also observed in evaporations in helium ambient. As would be expected, since helium has about one-tenth the mass of argon, an orientation effect occurs at a higher (1×10^{-3} mm) pressure than in argon (1×10^{-4} mm). The orientation effect observed at 5×10^{-5} mm in helium, {111}, suggests that a similar effect may be observed in argon at 5×10^{-6} mm. Palatnik and Komnik[5] have proposed that at sufficiently low pressures, atoms are deposited on an amorphous surface to form the crystal face having the highest reticular density. For tin-telluride this is the {111} plane. However, this evaporation was not attempted since the ambient pressure could not be so closely maintained during evaporation. The role of adsorbed or occluded ambient gases is suggested by the difference in orientation habit of the 1×10^{-4} mm argon film and the 1×10^{-3} mm helium film.

Effects of annealment atmosphere on film orientation

The anneals both in vacuum and in tellurium vapor were carried on at temperatures at which recrystallization should be expected to occur. This is verified by the increase in crystallite sizes after anneal. But the crystallite sizes show that if only growth of crystallites normal to the substrate is considered, no preferred orientation should be observed. The growth of preferred crystallites must therefore take place primarily in the plane of the substrate. The growth of differently oriented crystallites, in vacuum or in tellurium vapor, suggests that departure from stoichiometry may play a role in the regrowth habit. In a condition of stoichiometry or tellurium shortage (vacuum anneal) the film recrystallizes so as to close pack parallel to the substrate. However, if excess tellurium is present during regrowth, close packing in the substrate plane is inhibited. Regrowth of the {110} crystallites would allow inclusion of tellurium in the annealed film.

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Letters to the Editor

Properties of an Omegatron Tube Employing a Lanthanum Boride Filament

THE undesirable reactions occurring at the hot tungsten filament[1] of gauges and tubes attached to vacuum systems induced us to search for electron emitting sources which would operate at considerably lower temperatures. Previous investigators[1,2,3] reported the use of borides for cathode materials and we therefore equipped ion-gauges and omegatron tubes with lanthanum boride filaments. These were prepared by coating a small diameter tungsten wire, using an organic binder. For an ion-gauge running at a grid current of 100μA the filament temperature was between 750 and 800°C, compared to 1500–1600°C of a tungsten filament operating under the same conditions. The life of the filaments has been greatly increased, due to the low operating temperature. One gauge has continuously operated for approximately 1000 hr. During this time the system was exposed to the atmosphere for several days and was reactivated readily by simply flashing to 1400°C. The low temperature operation undoubtedly reduces the diffusion of boron into the tungsten, so that brittleness[2] does not become an important factor.

To study the effect of the LaB_6 on the residual gas composition, an omegatron tube having a lanthanum boride filament was attached to an ultra-high vacuum system. Prior to the measurements reported here the filament had been in constant use for about 200 hr. No effects due to outgassing were observed during this work. The UHV system incorporated a rotary forepump, two mercury diffusion pumps, an Alpert ionization gauge (having a tungsten filament), a Vac-ion pump and a Redhead magnetron gauge*. The omegatron tube, using molybdenum as the box material, was fabricated at Raytheon's Spencer Laboratory. Typical operating conditions were: electron current of 10μA, accelerating voltage of 50 V, collector and trapping voltages, 25 and 0.25 V respectively. The spectrometer's wide band oscillator and automatic scanner were an improved version of one previously described by Zdanuk *et al.*[4]

At a total pressure of 5×10^{-7} Torr with the system isolated from all pumps and only the omegatron tube operating, the spectrum of Fig. 1 was observed. The major peaks consisted of CH_4 and its derivatives and hydrogen. The presence of mass number m = 3 (H_3^+) was most interesting. The origin[5,6,7,8] of this ion could be either CH_4 or $H_2^+ + H_2$. It could not be due to a reaction at the Ti-surface of the ion-pump, because isolating this pump from the system did not affect the H_3^+ peak. Neither was it an " harmonic " or a " shadow " of another mass number ; peaks corresponding to m = 6 or 9 were absent altogether, the C^+ peak was always smaller than the H_3^+ peak and peaks due to H_2^+ and He^+ were too far away and too small to form a " shadow " the size of peak 3 (Fig. 2). The relative abundance of the CH_4 molecules, its derivatives and the lack of oxygen are most likely due to the organic binder in the LaB_6 filament. The use of non-reactive binders is feasible. Hickmott,[1] probably using an inorganic binder in his LaB_6 coated tantalum filament of his ion gauge, reported that the ratio of the peak CH_3^+ ion current to the peak H_2^+ ion current was 0.0002, measured in a 4×10^{-7} Torr hydrogen atmosphere. In our system and at an approximate partial hydrogen pressure of 1×10^{-7} Torr (Fig. 1) the value of the same ratio was 4. The major residual

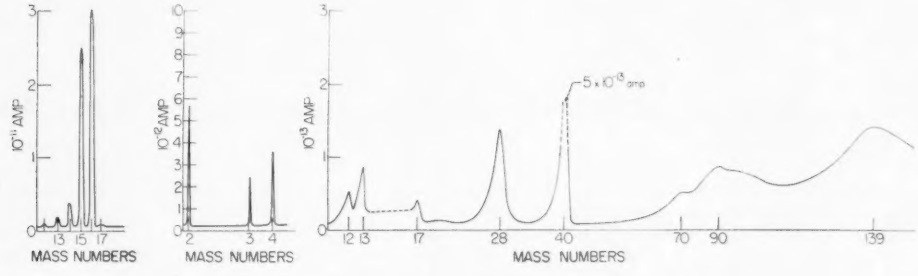

FIG. 1. Mass scan of residual gases at 5×10^{-7} Torr.

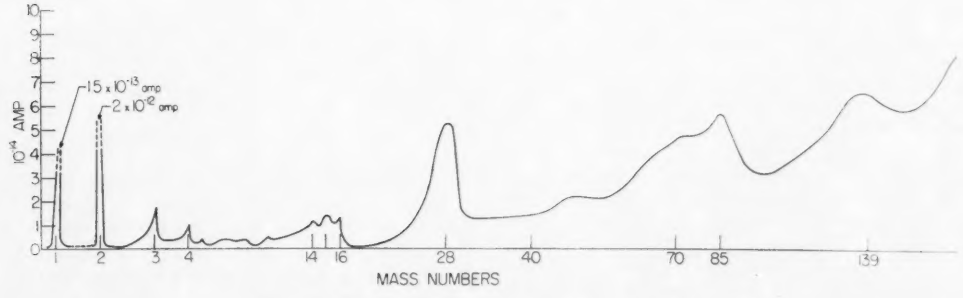

FIG. 2. Mass scan of residual gases at 5×10^{-8} Torr.

*Model 552, made by N.R.C., Newton, Mass.

gases in an UHV system containing tungsten filaments have been reported[7] to be CO–N_2 (m = 28) and H_2O (m = 17 and 18). Mass numbers smaller than 10 were not measured in that study. We have assumed for all ions quoted, except for $m \leqslant 4$, that since the ionization probabilities of the gases are very similar,[8] the peak omegatron current was proportional to the partial pressure. The ionization probabilities[8] for H_2^+ and He^+ are respectively about three and seven times smaller than that of CO^+.

When the pressure was lowered to 5×10^{-8} Torr by pumping either with one of the ion gauges or the ion-pump, the main masses recorded were H_2^+ and H^+ (Fig. 2). The other peaks observed were smaller by at least one order of magnitude. The peak at m = 70 was due to La^{++}, that at m = 96 probably due to Mo^+. The same spectrum was obtained irrespective of whether the ion-gauge was on or off, indicating that its tungsten filament had little effect on the residual gas composition. Lanthanum (m = 139) was present in the system at all pressures but boron was never observed. This is to be expected from the nature of the LaB_6 structure[2] where the boron forms a very strong framework through which the lanthanum diffuses, leaving the boron structure intact. No trace of water vapour was detected in the thoroughly baked out system. This appears to be in contradiction to the hypothesis of water formation by interaction of H^+ with the glass walls.[1] It is possible that the effective H^+ concentration was too low to produce a detectable amount of water or that the water disappeared through reaction with other constituents of the system. At the still lower pressure of 5×10^{-9} Torr, only H^+ and H_2^+ were clearly evident (3×10^{-12} A) with peaks due to m = 28, 40, 70 and 139 smaller than 5×10^{-14} A. Other investigators[4,7] reported that at this low pressure the residual gases in their system consisted mainly of CO and H_2O, with very small peaks at m = 16, 14 and 12.

Operating a lanthanum boride coated filament in UHV introduces the hydrocarbon CH_4^+ and its breakdown products into the system, but these are readily pumped off by any of the conventional ultra-high vacuum pumps. Ions of La^+ and La^{++} are also present and at roughly the same amount as CO^+, but less readily pumped off. As long as the operating temperature of the filament is kept below 800°C, the boron-structure will not break down and the filament's lifetime will be well over 1000 hr.

References

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Rapid Evaluation of Carbon Monoxide and Nitrogen Contributions to Mass Spectra

When a mass spectrometer is used for gas analysis on an ultra high vacuum system, the ion peak at a mass to charge ratio of 28 can be interpreted as N_2^+ or CO^+. Under certain conditions examination of the total ion pattern will not easily resolve the ambiguity, such as in the presence of CH_4 and CO_2. As a result the quantitative analysis of CO and N_2 in vacuum systems is not routinely made. This information can be important, however, when studying the neutral impurity background in gas discharges, filament reactions, or when simply concerned about a small leak.

We present here a particular choice of ion fragment peaks based on the gases commonly encountered in vacuum systems and a rapid method of converting the observed intensities of those selected peaks to the proportions of CO and N_2. With a vacuum system whose base pressure constituents are some combination of H_2, He, CH_4, H_2O, N_2, CO and CO_2 only, the CO and N_2 determination can be made from the peak heights at $M = 14$ and $M = 28$ after first correcting for the CH_4 influence on $M = 14$ and the CO_2 influence on $M = 28$. When the ion fragment pattern for each component is known this determination reduces to calculations of the form :

$$I(\mathrm{CO}) = 1.21\,I(28) - 17.24\,I(14) - 0.11\,I(44) + 1.95\,I(15) \quad (1)$$

$$I(\mathrm{N_2}) = -0.21\,I(28) + 17.24\,I(14) + 0.02\,I(44) - 1.95\,I(15) \quad (2)$$

which give the CO and N_2 contributions to the $M = 28$ peak height in terms of the measured total peaks at $M = 28$, 14, 15 and 44. The numerical coefficients are derived from the ionization patterns specific to the mass spectrometer, in this case the CEC Model 21–611. (The $M = 15$ peak is used as the CH_4 measure to avoid the $M = 16$ peak of H_2O).

The form of Equations (1) and (2) is such that a rather unique nomograph can be set up which permits a rapid evaluation of the CO and N_2 proportions during a mass spectrum scan. No computations are required and with an $8\frac{1}{2} \times 11$ in. chart two figure accuracy is possible.

In Fig. 1 an example is given where a dashed line between the total $M = 28$ peak value on scale A and the $M = 44$ value on C intersects B so as to give the " corrected " $M = 28$ value. Similarly a line between the total $M = 14$ value on scale H and the $M = 15$ value on scale F intersects scale G so as to give the " corrected " $M = 14$ value. A final line between these $M = 28$ and 14 values will intersect scales D and E at the numerical values of the CO and N_2 contributions.

The detailed procedure for constructing such a nomograph need not be presented. It is sufficient to point out that when two terms in an equation are to be added or subtracted the corresponding nomograph scales run in the same or opposite directions respectively. One starts by drawing the $M = 14$ and 28 scales in arbitrary positions and then constructs the

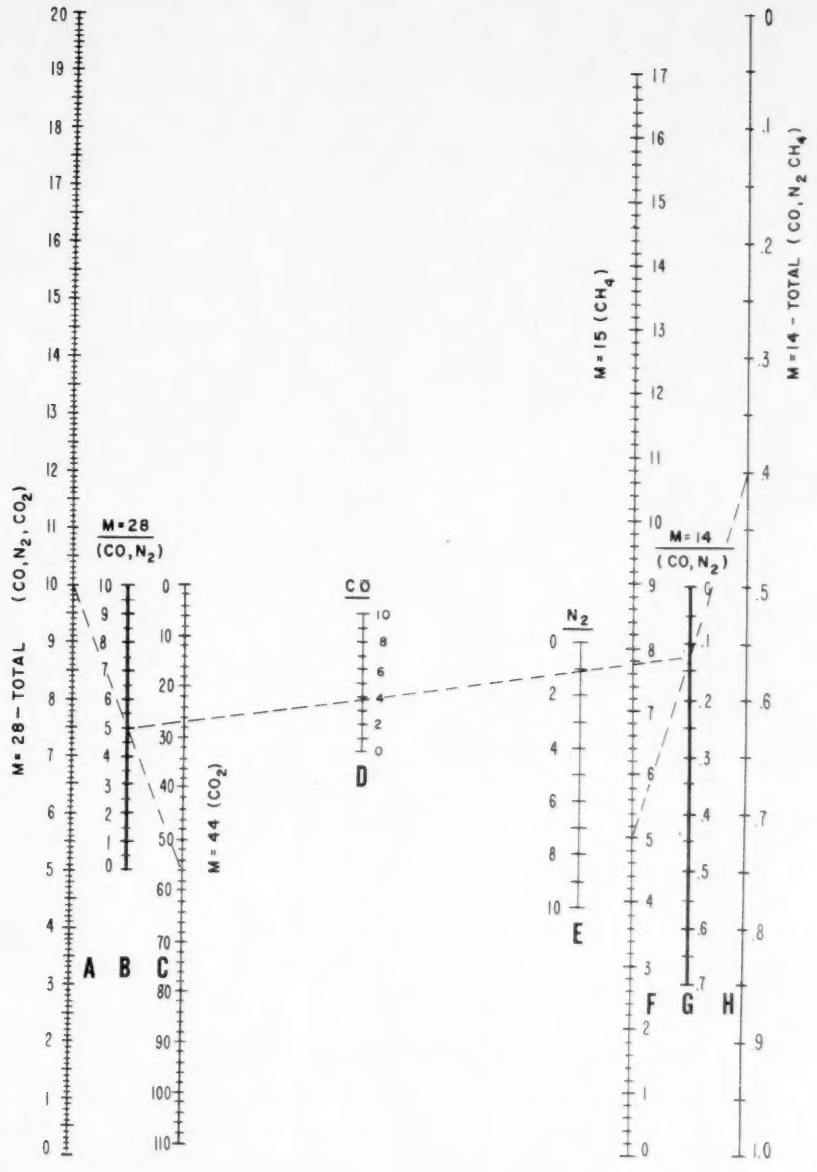

FIG. 1. Nomograph for rapid evaluation of nitrogen and carbon monoxide.

others after computing various special cases of CO, N_2, CO_2 and CH_4 concentration from Equations (1) and (2). It is hoped that with this particular example as a guide the extension to other mass spectrometers will be clear. In particular examination of the ion fragment pattern for the omegatron[1] reveals close similarities in the cases of CO, N_2, CH_4 and CO_2 to the pattern used here. Thus the same form of nomograph, with only small changes in the scale positions and calibrations is applicable.

Reference

[1] A. Klopfer and W. Schmidt; *Vacuum* **10**, 370 (1960).

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Note on Efficiency of the Vapour Vacuum Pump

ALTHOUGH attempts were made as far back as 1932[1] to define vapour pump efficiency, the problem is still in a state of confusion. This has led to some misunderstanding when comparing the results of different workers.

Theoretical considerations[2] led to the following expression of the speed S at the inlet port of the vapour pump

$$S = C\,\gamma\,(1-P_1/P) \tag{1}$$

where C is the conductance of the pump head (the chamber between the inlet port and the pumping aperture), γ is a factor smaller than unity indicating the imperfection of the pumping operation, and P_1 is the ultimate pressure.

Since

$$C = C_0 f_0, \quad f_0 < 1 \tag{2}$$

where C_0 is the conductance of the pumping aperture, and f_0 is the coefficient of conductance[3], one obtains from (1)

$$\epsilon = S/C = \gamma(1-P_1/P) \tag{3}$$

and

$$\epsilon_0 = S/C_0 = \gamma f_0(1-P_1/P). \tag{4}$$

Ratio $\epsilon_0 = S/C_0$ was suggested by Ho[1] as a criterion of pump performance. We shall term ϵ_0 speed efficiency. (3) and (4) give the physical interpretation of the coefficients ϵ and ϵ_0 showing, therefore, that three factors are involved in the working efficiency of the vapour pump: a geometrical factor f_0, an operational factor γ, and the ultimate pressure P_1. The difference between ϵ and ϵ_0 appears immediately from (3) and (4); the former, which we shall call pumping efficiency, shows the efficiency of the pumping action only, being independent of head conductance; the latter expresses the performance efficiency of the pump.

Taking into account (2) it follows that $\epsilon_0 < \epsilon$. It is then obvious that incorrect conclusions may be obtained if ϵ is confounded with ϵ_0.

Recently[4], there was reported a Ho coefficient of a vapour pump as high as 0.84 for air, a result indicating a considerable improvement of this instrument. But the factor calculated was nothing else than ϵ, as defined by (3). A coefficient of conductance $f_0 = 0.65$ having been measured, the speed efficiency was actually $\epsilon_0 = 0.65 \times 0.84 = 0.55$, value acceptable for a well designed pump.

References

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Conference

THE 39th Event of the European Federation of Chemical Engineering will be held in Athens from 31 May to 4 June 1962, and consists of the First European Symposium "Fresh Water from the Sea".

There are three Sections: (1) Evaporation Processes, (2) Electrodialytical and Related Processes and (3) Crystallisation Processes. Some of the papers presented will be of interest to Vacuum workers.

The address of the Secretariat of the Symposium is: Union des Chimistes Hellènes, P.O.B. 1199, Omonoia, Athens, Greece.

Abstracts

REPORT OF ABSTRACTING EDITOR

DURING the past three months an intensive effort has been made to improve the Classified Abstracts section of *Vacuum*. Readers can expect to see in 1962 a considerable increase in the number of abstracts presented. Many publications not previously covered will be systematically abstracted and it is hoped that by the end of the current year a substantial flow of literature from Eastern Europe and the Soviet Union will also be available.

A start has been made but much remains to be achieved. Many more abstractors are needed to scan the relevant journals. Vacuum workers who would like to help in this work are invited to write to the Abstracting Editor at the following address : *Vacuum*, Pergamon Press Limited, 4/5 Fitzroy Square, London W.1.

D. A. PREDDY

General Vacuum Science and Engineering

10. Vacuum Science and Technology

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221. The International Organization for Vacuum Science and Technology.

E. Thomas, *Vacuum*, **9**, 256–260, November 1959/January 1960.

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10 : 12

222. On the Choice of Units of Pressure and of Flow in Vacuum Technique.

Belgium. The various units of pressure and flow used in vacuum technique are examined. The use of a more adequate unit of pressure, related in a simple way to existing units, is proposed.

E. Thomas, R. Servranckx and R. Leyniers, *Vacuum*, **9**, 207–208, July/September, 1959.

10 : 11 : 12 : 20 : 21

223. Recent Advances in Ultra-high Vacuum Technology.

United States. The two major directions for advances in ultra-high vacuum technology are (1) the attainment and measurement of pressures below 10^{-10} mmHg, and (2) the development of large ultra-high vacuum systems. New vacuum components have recently been introduced which are of great value in both of these directions. Of particular interest are the development of ionization gauges capable of reading pressures below 10^{-12} mmHg and the design of systems several orders of magnitude larger than those heretofore described. Contributions of a number of workers in this field are briefly discussed. One of the most important recent developments is the " getter-ion " pump as a means of achieving both lower pressures and higher pumping speeds. It has been shown that very simple " getter-ion " pumps are possible which can replace diffusion pumps to achieve pressures down to the 10^{-10} mmHg region. Despite this achievement there are many unanswered questions involving the underlying mechanisms of sorption and desorption for neutral and activated molecular gases. Preliminary experiments have been made on the sticking probability of certain gases on titanium and the effect of an adjacent ionizing electron beam.

D. Alpert, *Vacuum*, **9**, 89–96, May 1959.

11. Production of Low Pressures

11 : 12 : 31 : 33 : 37 : 38

224. The Investigation of Residual Gases in Vacuum Systems.

United States. Considerable information has been obtained concerning the origin of residual gases in evacuated systems The experimental equipment involved in this research includes : (1) an omegatron mass spectrometer, (2) a sensitive quartz microbalance, (3) an apparatus for determining the adsorptive properties of getter films, and (4) associated vacuum systems. Preliminary data concerning the residual gas content of miniature electron tubes is presented. The application of the omegatron to the study of gases generated during tube processing and lifetime is outlined briefly.

S. P. Wolsky and E. J. Zdanuk, *Vacuum*, **10**, 13–22, 1960.

11 : 16 : 31 : 33 : 37 : 38

225. Evolution and Absorption of Gases in Electron Tubes.

United States. Gas-evolution effects in vacuum tubes have been determined by use of the gas-collection method of Morrison, in which evolved gases in an operating tube are collected with a mercury pump, stored in its fore-vacuum system, and measured with a mass spectrometer after many hours of tube operation. The speed of absorption of the tube for various gases has also been determined by simultaneously leaking gases into the tube and using the same collection system. In this way the partial pressures of gases and their internal evolution and absorption rates in the operating tube were found. These techniques were applied to a practical vacuum tube, the 21CYP22 colour-television picture tube. Typical partial pressures of gases determined during electrical operation of the tube were : hydrogen, 10^{-8} Torr; nitrogen (including a small fraction of carbon monoxide), 10^{-9} Torr ; and oxygen, 2×10^{-11} Torr. Oxygen is present only when the tube is scanned, and is evolved by non-metallic bulb surfaces which are bombarded with high-voltage electrons. Self-absorption of the tube for oxygen is very rapid (pumping speed is 3000 l/sec). Thus, oxygen partial pressure is maintained at such a low level during operation of this tube that there is no effect on performance of the oxide cathode.

R. H. Collins and J. C. Turnbull, *Vacuum*, **10**, 27, 1960.

11 : 12 : 37 : 38 : 22

226. Analysis of Partial Pressures by Means of Omegatron and Farvitron. Comparative View of the Ranges of Application.

Germany. The wide range of high vacuum technical problems, a solution of which may only be obtained by means of partial pressure analysis, is responsible for the fact that a variety of measuring methods becomes necessary. This applies in particular to sensitivity, pressure range, and rapid and comprehensive

response. The two partial pressure gauges—the Omegatron and the Farvitron (see paper given by W. Tretner, Darmstadt)—dealt with in the present paper are matching each other in an ideal manner. While the Omegatron having high sensitivity and good resolving power allows only the subsequent measuring of single partial pressures, the Farvitron gives a complete survey of the composition of partial pressures on an oscillograph. For this reason the Farvitron having less resolving power and lower sensitivity is highly suitable for indicating partial pressures especially during rapidly varying processes in the pressure range between 10^{-8} and 10^{-5} Torr.

G. Reich and F. Flecken, *Vacuum*, **10**, 35–39, 1960.

11 : 12 : 31 : 33

227. Residual Gases in Vacuum Systems.
Germany. Investigations of the gas composition in sealed-off high and ultra-high vacuum systems with the aid of the omegatron have shown that the gas evolution of the materials and interactions between the gases and the surfaces determine the kind of gases which are present. Such interactions are : adsorption, chemical and exchange reactions. The results obtained on radio tubes, TV picture tubes and systems consisting of glass and metal only are given in this paper. It appears possible to classify the composition of residual gases on the basis of the conditions prevailing in the systems in question.

A. Klopfer, S. Garbe and W. Schmidt, *Vacuum*, **10**, 7–12, 1960.

11 : 12 : 31 : 33

228. Residual Gas Pressure in Electron Tubes.
W. Dahlke and H.-J. Schütze, *Vacuum*, **10**, 3–4, 1960.

11 : 12 : 31 : 33

229. Residual Gas Pressure in Electron Tubes.
Germany. Results of measurement of the residual gas pressure in electron tubes are presented. These results were obtained during the processing and the life-tests of sealed-off tubes. The pressure is determined by using the electrode system of the tube itself as ionisation gauge. For easy observation of the pressure variations the collector current was recorded by an automatic recorder having a sensitivity of 10^{-12} amperes per scale.

H.-J. Schütze and H.-W. Ehlbeck, *Vacuum*, **10**, 5–6, 1960.

11 : 21 : 24 : 25 : 32

230. High-Vacuum Pumps and Units for Accelerators.
S. A. Vekshinsky, M. I. Menshikov and I. S. Rabinovich, *Vacuum*, **9**, 201–206, 1959.

11 : 16 : 18 : 21 : 22 : 47

231. Electrical Clean-up of Gases in Hot Cathode Discharge Tubes.
G. Carter, *Vacuum*, **9**, 120–200, 1959.

11 : 20 : 32

232. Vacuum System for a Thirty Billion Electron Volt Particle Accelerator.
United States. A vacuum system is being developed for a Thirty Billion Electron Volt Particle Accelerator. The vacuum chamber is a torus one-half mile in circumference with a cross-section of 3 in. by 7 in. Approximately fifty getter-ion type pumps will be used on the ring to give the required pressure of 2×10^{-6} mmHg. A linear accelerator yielding fifty million electron volts protons will be used as the injector. The vacuum chamber of this accelerator is 110 ft long and 3 ft in diameter. It will be evacuated to 1×10^{-6} mmHg by eleven getter-ion pumps. The choice of getter-ion pumps has permitted a departure from conventional vacuum system design and operation. Details of some new concepts of initial evacuation, steady state operation and simplicity of control of a system of this nature will be given.

C. L. Gould, *Vacuum*, **9**, 63–68, 1959.

11 : 20 : 21 : 25

233. The Production of Ultra-high Vacua by Means of a Diffusion Pump.
Netherlands. The result of a measurement of the so-called ultimate pressure of a diffusion pump is often not only determined by the pump itself, but also by the additional apparatus necessary for making this measurement. An analysis will be given of the gases which may be present at the pump mouth and the factors determining the pressure of those gases will be treated. A discussion of the methods which can be used for making these pressures as small as possible results in a design of a pump apparatus. A description of this apparatus, which includes a mercury diffusion pump with cooling traps, will be given. With the apparatus a pump speed at the recipient of 5–10 l/sec for the common gases is obtained and an ultimate pressure lower than 10^{-12} mmHg is reached.

A. Venema, *Vacuum*, **9**, 54–57, 1959.

11 : 21

234. The History of the Vacuum Pump.
United Kingdom. The first man to make a vacuum pump was Guericke, somewhere about 1654. It was a crude pump, with joints kept airtight by water immersion. Soon after Boyle produced a much improved piston pump, made by Robert Hooke. About the same time the Accademia del Cimento used the vacuous space in the enlarged head of a mercury barometer to carry out experiments : this may be considered as a one-stroke mercury pump. Pumps on the Boyle pattern were made by Huygens, Papin and Senguerd. In 1682 Boyle described a two-cylinder pump, in which the pressure of the atmosphere on one piston did most of the work required to raise the other. A much improved pump of this type was made by Haukesbee about 1705 and this remained essentially the pattern of cylinder vacuum pumps until the end of the nineteenth century, when Fleuss introduced the cylinder oil pump. For producing high vacua for the classic research on discharge in gases, pumps of the Geissler and Toepler type, based on continuous repetition of Torricelli's experiment, were used, which were extremely slow in action. A new era was initiated in 1905, when Kaufmann introduced a continuously rotating mercury pump, which was almost at once superseded by Gaede's much speedier rotary mercury pump. Fore pumps of box type, the prototypes of which were water-pumps of the sixteenth and seventeenth century, were brought in by Gaede and others. In 1912 Gaede invented a pump based on a fundamentally new principle, that a surface moving rapidly parallel to itself drags with it gas molecules. This so-called molecular pump produced extremely low pressures. The last inventive step was also made by Gaede, when in 1915 he utilized the carrying along of gas molecules by a jet of mercury vapour to effect a high vacuum. These vapour-stream pumps, oil and mercury, have been developed on an enormous scale of recent years. (Author)

By E. N. da C. Andrade, *Vacuum*, **9**, 41–47, 1959.

11 : 10 : 12 : 20 : 21

Recent Advances in Ultra-high Vacuum Technology. See Abstr. No. 223.

12. Measurement of Low Pressures

12 : 22

235. A McLeod Manometer with Prescribed Volumes for Use as a Standard Instrument.
Netherlands. The McLeod manometer is one of the few instruments with which it is possible to measure the actual values of low gas pressures ($5–10^{-5}$ mmHg) without changing the composition of the gas. The McLeod gauge is therefore indispensable for calibrating the faster indicating instruments which only register relative pressure units, e.g. ionization gauges, heat-conductivity manometers, etc. Since it is very cumbersome to

make and calibrate a McLeod gauge that can be used as a standard, it is worthwhile to improve the construction in such a way that a calibration can be omitted. In connexion with this problem a critical study was made of the formulae used to calculate the gas pressure from the readings of the McLeod manometer, which lead to expressions for the relative systematic and accidental errors limiting the measuring accuracy. By using a very accurate set of jigs in making the capillaries and the transition volumes at the connexion between capillaries of different diameters and by addition of a small correction volume to the compression bulb it was possible to construct a McLeod gauge indicating the actual gas pressures in the range of $3.5–10^{-5}$ mmHg on one convenient set of scales. The volume of the compression bulb and the volume and diameters of the capillaries were calculated in such a way that full centimetres on the various scales correspond to 10^{-3}, 10^{-2} and 10^{-1} mmHg respectively. The zero lines of the different sub-ranges of the instrument lie at whole centimetres from each other and at multiples of half-centimetres from the top of the compression capillary. (Authors)

C. G. J. Jansen and A. Venema, *Vacuum*, **9**, 219–229, 1959.

12 : 31 : 33 : 47

236. Emploi du Spectromètre de Masse dans la Technologie des Tubes Électroniques.

France. After mentioning the interest of using a mass spectrometer for the study of some fundamental problems raised by the technology of the electronic tubes, the author recalls and discusses the characteristics and performances required of the spectrometers to be used in the best conditions for the quantitative analysis of the residual gases, the study of their origin and influence (especially on the cathodes behavior). In order to have valid measurements, the inner structure of the analyser tube must not modify the composition of the analysed gas ; in other words, it must not have any internal residual gas. Therefore, the spectrometer must have reduced dimensions and the smallest possible surface effects, and it must be possible to outgas the tube energetically. These requirements usually exclude the use of classical sector field spectrometers and limit our choice to transit time spectrometers or radio frequency mass spectrometers. Two types of spectrometers which can be used with profit are described : the Omegatron and the Bennett type analyser. The compared performances and characteristics of these two devices show that their qualities are complementary and that their simultaneous use can allow to perform the analysis concerned, both for static or rapidly varying phenomena, within a convenient range of pressure and mass. (Author)

R. J. Warnecke, Jr., *Vacuum*, **10**, 49–57, 1960.

12 : 22

237. The Measurement of the Pressures of Various Gases by means of a Pirani Gauge.

Czechoslovakia. The relation between the gas pressure and the potential difference existing across the diagonal of the Wheatstone bridge, E_{12}, which is a function of pressure, has been determined for a Pirani gauge. Using this relation, calibration curves for various gases may be calculated from Pirani gauge calibration curves for a given gas. (Author)

S. Veis, *Vacuum*, **9**, 186–189, 1959.

12 : 16 : 21 : 22

238. Initial Pumping and Recovery of Ionization Gauges.

United Kingdom. Measurements have been made on the pressure decrease in a closed glass system when an ion gauge pumps and also of the recovery of pressure when pumping is stopped after a short period. The pressure decrease may be represented by an equation of the type $p - p_1 = C_1e^{-a_1t} + C_2e^{-a_2t}$ where p and p_1 are the pressure after any time t and the "final" pressure, respectively. C_1, C_2, a_1, a_2 are parameters depending upon the nature of the gas and surfaces. For pumping a_1 and a_2 contain terms depending upon the electron current. For recovery a_1 is determined by the sticking time of pumped molecules on the glass and a_2 by a glass characteristic. Average sticking times are found to increase from about 10 to 2000 sec. as the temperature of the system increases from 22 to 450°C with consequent change in heats of adsorption from 18 to 40 kcal/mole approximately. The increase in sticking times are attributed to changes in residual gas composition. (Authors)

N. W. Robinson and F. Berz, *Vacuum*, **9**, 48–53, 1959.

12 : 10

On the Choice of Units of Pressure and of Flow in Vacuum Technique. See Abstr. No. 222.

12 : 10 : 11 : 20 : 21

Recent Advances in Ultra-high Vacuum Technology. See Abstr No. 223.

12 : 11 : 31 : 33 : 37 : 38

The Investigation of Residual Gases in Vacuum Systems. See Abstr. No. 224.

12 : 11 : 37 : 38 : 22

Analysis of Partial Pressures by Means of Omegatron and Farvitron. See Abstr. No. 226.

12 : 11 : 31 : 33

Residual Gases in Vacuum Systems. See Abstr. No. 227.

12 : 22 : 31 : 33 : 38 : 37

The Applicability of the Omegatron to Continuous Analysis of Residual Gases. See Abstr. No. 291.

12 : 31 : 33 : 22

An Electrostatic Mass Spectroscope. See Abstr. No. 311.

12 : 11 : 31 : 33

Residual Gas Pressure in Electron Tubes. See Abstr. No. 228.

12 : 11 : 31 : 33

Residual Gas Pressure in Electron Tubes. See Abstr. No. 229.

14. Kinetic Theory of Gases

14 : 21

239. The Theoretical Development of the Vapour Vacuum Pump.

Australia. The empirical development of the vapour pump led to the rejection of such phenomena as diffusion or condensation as the only processes involved in the function of this instrument. Further theoretical attempts which ignored the action of the vapour jet in producing a high vacuum have failed to correctly interpret the experimental results. By considering the removal of the gas molecules by the vapour stream as the basic process, a satisfactory theory of the vapour pump has been obtained. The theoretical conclusions were able to describe the working mechanism of the pump, to explain a large variety of experimental results, and to indicate the proper way of achieving design improvements. (Author)

N. A. Florescu, *Vacuum*, **10**, 250–259, 1960.

16. Gases and Solids

16 : 47

240. Some Reactions of Water in Electron Tubes.

Germany. During pumping of tubes a great part of the present gases is formed by water, which desorbs from the surfaces and is also evolved from various materials, especially from glass and mica. For a short outgassing time the evolution of water from the surface of the glass prevails, resulting in a decrease of the surface coverage with water. In sealed-off systems water vapour undergoes various reactions, as : adsorption on the surfaces ;

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reactions with the hot cathode, leading to formation of H_2, CO_2, CO and CH_4 ; and reactions at the barium getter mirror, giving H_2 and CH_4. After flashing the getter an amount of 8×10^{-3} Torrl water had been introduced into a television picture tube, resulting in a far higher level of H_2, CH_4 and CO_2 than in normal processed tubes even after 180 hr life and operation. The H_2O pressure, however, had decreased from above 10^{-5} Torr to 4.10^{-9} Torr. Generally we may conclude, that an increased water evolution in tubes leads to a higher residual pressure of H_2, CH_4 and CO_2 during life. (Authors)

S. Garbe, A. Klopfer and W. Schmidt, *Vacuum*, **10**, 81–85, 1960.

16 : 21 : 20

241. The Gas Sorption Characteristics of Penning Pumps and Titanium Films.

United Kingdom. The gas sorption characteristics of evaporated Ti-films about 100 Å thick and of a Penning pump with titanium electrodes have been studied and compared. The Penning pump also served as an ion-source with the Ti-films. The sorption apparatus consisted of a bakable stainless steel getter chamber of 1400 cm^2 area and a Penning pump of 75 mm diameter. The vacuum seals were made with metal gaskets and the pressure measured with a hot filament ion-gauge. The gas to be sorbed was admitted to the getter chamber from a reservoir via a calibrated leak. Sorption rates were measured in the pressure interval 0.001–1 μHg. The pumping speed of an evaporated Ti-film alone was negligible (<0.1 l/sec), but greatly enhanced when the Penning ion-source was in operation as previously found by Gale. Inert gases were only sorbed by the Penning pump. Instantaneous speeds measured at 10^{-6} Torr for fresh Ti-films with the ion-source in operation were, in l/sec., as follows : Air, 56 ; N_2, 56 ; O_2, 56 ; H_2, 234. When the sorption rates of either the Penning pump alone or the Penning pump with a Ti-film were plotted in terms of mass sorption rates (litre microns/sec) as a function of pressure it was found that the resultant curves were parallel to the ionization current/pressure curve of the Penning discharge, i.e. the mass sorption rate at a given pressure was directly proportional to the discharge current at that pressure. The sorption characteristics of mixed gases were studied to find the effect of one molecular type on the clean up of another. It is shown that the sorption rate of hydrogen is reduced by the presence of organic vapours, e.g. methane. Sorption rates were also measured for gas mixtures of argon/hydrogen, and nitrogen/" Calor " gas (butane). Measurements were rendered difficult when using hydrocarbon/gas mixtures due to the uncertainty in determining the sensitivity factor to be used with the ion-gauge. The role of ionization in enhancing the gas sorption rate is discussed by Holland in an appendix. The increase in the rate of clean up by titanium was not due to ions flowing to the film because the getter chamber was at a positive potential. The high sorption rate of H_2, O_2, and N_2 when ionized was attributed to their atomization in the Penning discharge. Thin films of titanium are composed of densely packed grains and the enhanced rate of clean up is attributed to the atomic gas being able to penetrate the interstices between the grains and reaction products on the porous film. (Authors)

L. Holland and A. Harte, *Vacuum*, **10**, 133–140, 1960.

16 : 33

242. Method for Ageing of Electron Valves.

O. Pressel, *Vacuum*, **10**, 141–142, 1960.

16 : 21 : 33

243. Test of Use of Titanium as Getter.

France. It seems interesting to do some absorption tests of residual gas in replacing in the tubes with oxide cathode, the getters ordinarily used by titanium pieces of simple form. The described tests concern 2 special types of tubes : a miniature 3B4, with beam tetrode whence the realization (setting up and pumping) is rather difficult, taking into account of the imposed performances ; an experimental oscillator miniature tube chosen, particularly, in reason of its small volume. The metal used was pure titanium. In a first series of tests, we eliminated completely barium getters and the fixation of residual gas has been assured by the presence of titanium anode instead of conventional nickel anode. In a second series of tests, we searched to replace the barium getter by one simple piece of small dimensions in pure titanium ; small disc of titanium sheet or rings in titanium wire of 1 mm in diameter. These pieces were heated by R.F. after exhausting and tip off. These diverse tests permitted to notice the efficiency of the titanium used directly as getter : the ageing process is very soft and does not make any metallic projection on the inner side of the bulb, that eliminated some possible defects (inter-electrode leakage, noxious capacitances). (Author)

J. M. Sourdillon, *Vacuum*, **10**, 166–169, 1960.

16 : 21 : 41

244. Gettering Activity of Zr, Ti and Ba for Oxygen Gas under the Mercury Vapour.

Japan. The absorbability of oxygen gas in barium, titanium and zirconium is known, but when mercury vapour is simultaneously present this influences seriously the absorbability of oxygen gas in Mercury Vapour Hot Cathode Tubes containing mercury vapour. An easy method for the measuring of getter activity in oxygen gas under mercury vapour is to measure the electrical conductivity of the oxide layer of the oxide cathode. This is that the oxide cathode itself is a semiconductor of excess Ba metal type, and the comparison relation with the pressure of its exterior oxygen (in this case oxygen inside the tube) has been utilized. For this purpose, an oxide part has been coated over the pure nickel sleeve, and over this a pure nickel wire is wound as a probe. The electrical conductivity of these two poles is measured at a regulated temperature. The mixed oxygen and mercury vapour inside the tube is measured by the increase-decrease of oxygen. By this method, the absorbability of oxygen has no change in titanium and zirconium even in presence of mercury vapour, but in regard to barium, in presence of mercury vapour, this latter amalgamates with mercury vapour and thus the previously absorbed oxygen is freed. (Author)

S. Fukagawa, *Vacuum*, **10**, 178–180, 1960.

16 : 21 : 22

245. Apparatus and Techniques for Measurements of the Adsorption of Gases by Evaporated Getters.

Italy. The present work describes the apparatus and techniques used at the S.A.E.S. Research Laboratories to study the gettering action of evaporated barium films on different gases. During the past few years the sorption of gases by getters (evaporated or not) has been increasingly studied from a kinetic approach, by techniques capable of giving a direct measurement of the velocity of sorption. Kinetic measurements can be effected either by measuring the fall of pressure with time in a sealed container of known volume, or by estimating the gas flow through a capillary of known conductance. The latter method can be applied by keeping the manifold pressure constant and allowing the getter pressure to vary with time, but more useful results can be obtained when the pressure on the getter is kept constant. Measurements at constant p_m are by us usually confined to preliminary large scale investigations. For such measurements suitable apparatus and automatic pressure recordings are used, which enable us to carry out more than one test at the same time. For sorption studies at very low pressures, the normal apparatus is attached to an ultra high vacuum system. The experimental results obtained by measuring the gas flow at constant p_g, when suitably interpreted, allow us to study the complex sorption mechanism, showing the existence of diffusion phenomena, giving useful indications about the mobility of molecules on the surface and within the film and permitting the evaluation of the activation energy of different processes. Suitable apparatus enables us to study the influence of hot filaments and ionizing electron currents in the vicinity of the getter. A knowledge of these effects is in fact

necessary for a correct evaluation of the data obtained for sorption velocities by using ionization gauges and permits these effects to be kept at a minimum in the experimental procedure. Further suitable apparatus is employed to study other parameters which may effect the activity of barium getters, such as the time of flashing, the pressure immediately preceding the firing of the getter, the distance and temperature of the surface on which the film is formed. In particular such devices permit the study, by electron microscopy, of the structure of the barium films obtained under various conditions. Finally, the recent introduction of mass spectrometers of reduced dimensions and able to measure very low partial pressures (e.g. the omegatron), enable us to confirm the eventual chemical processes occurring on the varium film (catalytic reactions) and also it opens a way to the study of getter action on gaseous mixtures. (Author)

P. della Porta, *Vacuum*, **10**, 181–187, 1960.

16 : 21 : 22

246. An Automatic Apparatus for the Testing of Getter Adsorption.

England. Routine testing of getter films has in the past been carried out using dosing methods, which require the constant attention of an operator. An apparatus has therefore been developed which operates automatically, recording the uptake of gas and at the same time maintaining the gas pressure over the getter constant. The principle of operation is as follows. Pulses of gas enter the getter chamber from a reservoir through a special magnetic valve which is continuously and rapidly opened and closed. The ratio of time open to time closed is automatically controlled so as to maintain a constant pressure in the getter chamber. Control is exerted by a special switching circuit which continuously varies the ratio of interval on to interval off, according to the input signal. This signal is provided by the voltage across the meter in the getter chamber Pirani gauge circuit. With a Pirani gauge attached to the gas reservoir, a continuous record of pressure drop against time can be obtained with a potentiometer recorder. If a capillary tube and high pressure Pirani gauge are interposed between the getter chamber and the magnetic valve, the signal from this Pirani gauge may be used to obtain a direct record of gettering rate against time. The apparatus has been used with carbon monoxide and hydrogen at getter chamber pressures of about 1μ. There is no limit with regard to the use of higher pressures, but with the present control circuit the use of lower pressures would lead to less satisfactory control, which at 1 micron pressure was never worse than ± 10 per cent, and generally much better. (Authors)

M. G. Charlton, D. Newson and P. J. Whitchurch, *Vacuum*, **10**, 189–193, 1960.

16 : 21 : 33

247. The Influence of Ionizing Electron Currents and Hot Filaments on the Gas Adsorption by Barium Films.

Italy. In studying the effect of ionizing electron currents on the sorption of gases by getters, it is necessary to distinguish between: (a) the pumping action of the hot filament and of the ionizing current, and the sorption by the getter; (b) the gettering of activated particles and usual gettering of gaseous molecules. Bloomer has pointed out how the activating action of the ionizing electron current is to be added to the normal gettering by barium films. This criterion has been applied in all our work on the various phenomena mentioned previously: normal gettering, electrical clean-up, pumping effect of the hot filament and gettering of activated particles. By using an analogous additive principle, it is still possible to employ an ionization gauge of the Alpert type to measure the pressure, even when studying the effects of an ionizing electron current, by falling back on supplementary electrodes and tubes for a study of the other parameters. The measurements have been carried out employing the capillary technique at constant pressure on the getter. The apparatus used in these experiments is obtained by simple modifications of devices already described in previous communications. Such modifications introduce, on the getter side of the capillary, supplementary tubes with the required electrodes. With such devices we have carried out a number of tests to compare the velocity of pumping with and without getters, in various gases, when altering temperature and size of the surface and the intensity and energy of the ionizing electron beam.

P. della Porta, S. Origlio and E. Argano, *Vacuum*, **10**, 194–198, 1960.

16 : 21

248. The Absorption of Gases by Barium Getter Films applied as a Tool.

Netherlands. Some means will be discussed by which all barium-alloy getter types may be compared. Both the " melting-curve " and " yield-curve " of a getter type will give full information on its properties during flashing. From them the reliability of the getter may be read. Further a hydrogen- and/or oxygen-capacity measurement can be used to check for contamination in the barium film produced. An additional investigation on the CO-capacity will inform on the active area of the film, which usually will be larger than the area of the surface covered by barium. The method will be explained by applying it both to a radio-valve getter and to a television-getter. (Authors)

J. J. B. Fransen and H. J. R. Perdijk, *Vacuum*, **10**, 199–203, 1960.

16 : 41 : 21

249. The Adsorption of Methane by Barium Films in the Presence of a Thermionic Current.

United Kingdom. The adsorption of methane at pressures of 7×10^{-7} to 7×10^{-6} Torr has been studied both in the presence and absence of a thermionic current drawn from a tungsten filament, using the capillary flow method of Wagener, and maintaining the pressure over the barium film constant. The pumping speeds of barium films covering up to 160 cm^2 and up to 20 mg in weight under normal conditions were very small and were less than 5 cc/sec at 1.5×10^{-6} Torr. The presence of an incandescent tungsten filament caused a slight increase in pumping speed of the barium films of about 10–20 cc/sec. Drawing an emission current from the filament appreciably increased the pumping speed of the getter, the increase amounting to 70–100 cc/sec at 1.5×10^{-6} Torr with a current of 5 mA. The pumping speed was independent of the area and weight of barium film but was approximately proportional to the thermionic current; it was almost independent of the pressure, up to 7×10^{-6} Torr, and hence the adsorption rate (pumping speed $\times$ pressure) was roughly proportional to pressure. The results show that the adsorption rate on barium films of methane activated by electron impact is determined entirely by the frequency of electron-gas molecule collisions. It is not known whether the active species consists entirely of ions or whether non-ionized radicals and molecules resulting from the decomposition of methane are involved. (Authors)

M. G. Charlton and F. H. Southam, *Vacuum*, **10**, 212–214, 1960.

16 : 41 : 30 : 21

250. Carbon Monoxide Sorption by Barium Films.

Italy. A number of workers have in the past few years studied carbon monoxide sorption by barium films, often obtaining diverging results. The complex nature of the problem, which cannot be considered as a simple surface adsorption, is shown by the work of Arizumi and Kotani, who propose a model based on the existence of lattice imperfections in the barium film and also by the work of Bloomer who applies to this phenomenon the Mott–Cabrera theory for oxidation of metals. The problem is here considered in view of the results obtained by the capillary technique at constant pressure on the getter. The experiments have been carried out in the temperature region between 195°K and 473°K. The kinetics of sorption may be studied and an analysis of the mechanism of the process may be undertaken from the obtained data. The initial velocity of the

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adsorption is approximately the same at the various temperatures at which the experiments were carried out, and remains nearly constant for an interval of time which increases with increase in temperature. The decreasing part of the sorption velocity curve can be interpreted as due to a diffusion phenomenon. The initial part of the curve at constant velocity, which is characteristic of carbon monoxide sorption by barium, had been often misinterpreted and attributed to the limited conductance of the capillary, and so considered non relevant to an explanation of the phenomenon. In agreement with the work of the previously mentioned Japanese authors, we recognized the value of this result, which depends on the fact that various processes are involved in the phenomenon, each one rate determining according to the pressure and temperature prevailing and according to the quantity of gas already sorbed by the getter. The whole phenomenon is thought to be due to an initial adsorption on the surface and to a subsequent surface diffusion having a low activation energy or, at sufficiently high temperatures, to a bulk diffusion, which is characterized by a higher activation energy. The end of the constant velocity portion of the curve is thought to be related to the instant when the diffusion becomes slower than the surface adsorption. The evaluation of the energy of activation for the diffusion phenomenon reveals the existence of a critical temperature in the neighbourhood of 373°K. (Authors)

F. Ricca and P. della Porta, *Vacuum*, **10**, 215–222, 1960.

16 : 21 : 33 : 41 : 30

251. Nitrogen Sorption by Barium Films.
Italy. In previous communications nitrogen sorption on barium films having a mean thickness of 0.02 mg/cm², has been reported. This thickness had in fact been adopted to facilitate the reproducibility of results. The study of the sorption by the capillary method under Knudsen flow conditions and at constant pressure on the getter, has enabled the identification of an initial adsorption on the getter surface directly exposed to the gas, and of subsequent diffusion processes within the film, which are characterized by two different activation energies, below and above 413°K. The present work tends to prove the applicability of such a model in the case of film thicknesses encountered in the manufacture of electron tubes (about 0.2 mg/cm²). Still looking at the problem from the tubes manufactures point of view, the influence of the time of flashing of the getter on the sorption velocity for nitrogen is examined. The time of flashing is varied, in this series of experiments, from 4 to 40 sec. The influence of the residual pressure previous to the flashing of the getter is also examined in the pressure range from 10^{-6} to 10^{-3} Torr. Finally it should be noted that examining the data obtained for the sorption of nitrogen on films of different thickness, as well as from the comparison of such data with similar results for carbon monoxide and hydrogen previously reported, it would appear that parallel mechanisms may be identified in the sorption of a number of gases by barium films. (Authors)

P. della Porta and E. Argano, *Vacuum*, **10**, 223–226, 1960.

16 : 21

252. Hydrogen Sorption by Barium Films.
Italy. The capillary method, under Knudsen flow conditions and at constant pressure on the sorbent, is in this work applied to the study of hydrogen sorption on evaporated barium films. Particular precautions have been taken to reduce to a minimum the influence of the hot filament and electron current of the ionization gauge (Alpert type) on the measurement of the sorption velocity. To this end, thoriated tungsten filaments have been employed and very low ionizing electron currents (0.01 mA) have been used. The experimental results have been obtained in the temperature range between 195 and 473°K, on barium films of approximately 2 mg, evaporated from a stabilized barium-aluminium alloy and having an apparent surface area of 100 cm². A preliminary investigation of the curves giving velocity of sorption as a function of time, shows that the shape of such curves is dependent on the pressure range in which they are obtained. At the higher pressures the kinetics of adsorption follows very closely the diffusion laws, as is shown by the nearly linear relation existing between quantity sorbed and square root of time. On the other hand at lower pressures, the graphs show an almost horizontal portion, corresponding to a constant velocity of sorption lasting a considerable period of time. These differences in behaviour show that for hydrogen, as for other gases, the sorption by barium films is made up of a number of phenomena superimposed on each other. The different appearance of the various phenomena for different gases can, with all probabilities, be attributed to the different coefficients of diffusion of the gases and the relative activation energies. (Authors)

P. della Porta and S. Origlio, *Vacuum*, **10**, 227–230, 1960.

16 : 21

253. On the General Principles of Chemical and Ionic Pumping.
United Kingdom. As a start some differences between physical and chemical adsorption are emphasized. The distinction between chemical and ionic pumping is defined and discussed, and examples quoted, both recent and historical. Since in getter-ion pumps different kinds of gases have to be handled simultaneously, examples are mentioned where the presence of some gases is known to greatly influence the kinetics of adsorption of other particular gases. In any case, the interpretation of the readings obtained when checking pump performance is hazardous when gases of differing condensation coefficient are present together. A simple test that measurements are well-founded is described. Some surface reactions that can limit the performance of getters, and ways of possible improvement, are suggested. (Author)

R. N. Bloomer, *Vacuum*, **10**, 260–262, 1960.

16 : 21

254. Physical Processes in Small Titanium Ion Pumps.
United Kingdom. Experiments with small ion pumps in which titanium is continuously deposited are described. Two types were investigated, the first being a conventional thermionic ionization gauge with titanium evaporating from a directly heated source in the envelope and the second a Penning type of discharge tube in which titanium was sputtered from the end plates. In the first type all the gases and vapours tested were pumped by ion burial and all except argon were also pumped by adsorption onto the already deposited titanium film and then covered by the arriving titanium. In addition the hot tungsten could combine chemically with oxygen and also convert hydrogen into the atomic form which was then able to diffuse into the titanium. Water vapour and organic vapours were also decomposed by the hot tungsten. In the Penning discharge pump the speed of pumping was constant for each gas over a wide range of pressures, and depended on the titanium sputtering rate and rate of adsorption of the various gases. It was found that appreciable desorption of pumped gases took place in the sputter-ion pump but could be made negligible in the evaporation-ion pump. (Authors)

R. O. Jenkins and W. G. Trodden, *Vacuum*, **10**, 319–328, 1960.

16 : 31 : 33 : 47

255. The Action of Molybdenum, Tungsten, Tantalum and Nickel on Residual Gases in a Vacuum System.
United Kingdom. The interaction between the above metals and residual gases in a vacuum system is studied by flash filament and mass spectrographic techniques. The chief action occurs with carbon monoxide and the metals molybdenum and tantalum. Critical flash temperatures are found below which residual carbon monoxide is diminished and above which it is increased. The effect of sputtered and evaporated films of the metals on glass is also described. (Author)

N. W. Robinson, *Vacuum*, **10**, 75–80, 1960.

16 : 36 : 47

256. Clean Surfaces and Sorption of Gases.
Italy. Chemisorption studies have progressively shown the importance of having available truly clean surfaces to obtain valuable results. To this end in the past few years extensive use has been made of evaporated films : however, recent trends seem to prefer the use of bulk materials (filaments, foils, tips) which can be degassed at high temperature. Such materials are much more versatile than films, and give a useful basis to the development of new techniques for the study of surface phenomena. These surfaces can be used any number of times ; they further permit the elimination of secondary phenomena, not strictly related to the surface, such as diffusion within the discontinuous structure of evaporated films. Techniques employing bulk materials are necessarily restricted to those metals which do not possess an appreciable vapour pressure at the degassing temperatures required. However, the results which have recently been obtained with this type of sorbent, by field emission microscopy, field ion microscopy and flash filament technique, are of great theoretical interest and can be applied to most of the other metals. We limit ourselves to quote the information obtained about the existence of : (a) various types of atoms on the metal surface, characterized by different sorption properties ; (b) different coefficients of surface diffusion for the different crystal faces ; (c) different states of the gas adsorbed on the metal. Concerning this latter point, useful information can be obtained from infrared spectroscopy of the adsorbed molecules. This complex picture of the observed phenomena is confirmed by our results for the adsorption of nitrogen and carbon monoxide on tungsten. The technique used to measure the velocity of adsorption, based on the flow of gas through a capillary of known conductance, is similar to that used in the field of getters ; the adsorbent is a tungsten lamina having a thickness of 0.0025 cm and a surface area of 27.5 cm^2 ; the measurements have been carried out in the pressure range of 10^{-7} to 10^{-8} Torr, and in the temperature interval between 90 and 480°K. A problem of particular interest arises from the immeasurably low temperature coefficients and from the fact that the velocity of adsorption is initially independent of the surface coverage. The theoretical hypotheses put forward concerning this problem are briefly examined. The correct interpretation of such complex surface phenomena seems to be necessary even for the study of gas sorption by evaporated metal films. (Authors)

A. Nasini, F. Ricca and G. Saini, *Vacuum*, **10**, 68–74, 1960.

16

257. Adsorption of Water and Polar Paraffinic Compounds onto Rutile.
C. M. Hollabaugh and J. J. Chessick, *J. Phys. Chem.*, **65**, 109–114, January 1961.

16

258. The Exchange of Deuterium Gas with the Hydrogen Associated with Solid Catalysts. II. Kinetics and Mechanism of the Reaction with Hydrogenated Tantalum.
W. K. Hall, W. E. Wallace and F. J. Cheselske, *J. Phys. Chem.*, **65**, 128–132, January 1961.

16

259. Thermodynamics of Water and n-Butane Adsorption by Li-Kaolinite at Low Coverages.
J. J. Jurinak and D. H. Volman, *J. Phys. Chem.*, **65**, 150–152, January 1961.

16

260. The Effect of Pretreatment on the Adsorption and Desorption of Water Vapor by Lithium and Calcium Kaolinite.
United States. The adsorption and desorption of water vapor by lithium and calcium kaolinite degassed at 33, 70, 100 and 205° was studied. Li-kaolinite degassed at 33 and 70° resulted in the reversible adsorption-desorption of water vapor. Hysteresis became prevalent at the higher degassing temperatures. Reversible dehydroxylation was considered initiated at 205°. Ca-kaolinite adsorbed more water and hysteresis was noted at all pretreatment levels. Factors considered important in the variability of water adsorption by Li- and Ca-kaolinite, in the degassing temperature range studied, are ionic hydration, particle coalescence and surface dehydroxylation. (Author)

J. J. Jurinak, *J. Phys. Chem.*, **65**, 62–64, January 1961.

16

261. High Temperature Adsorption Studies on 13X Molecular Sieve and Other Porous Solids by Pulse Flow Techniques.
United States. The adsorptive properties of solids at high temperatures are conveniently studied by allowing a pulse of adsorbate to be transported through a packed column of adsorbent by an inert carrier gas stream. The concentration of adsorbate in the effluent stream is continuously measured by a sensitive thermal conductivity cell. Modifications of such a technique permit the detection of an adsorption process and enable one to determine its degree of reversibility. In addition, heats of adsorption can be determined by measuring the pulse retention times at a series of temperatures. This flow method is particularly useful for studying adsorption at high temperature conditions where static methods cannot be used because of the long contact times involved which lead to decomposition of the adsorbates. In this manner, it has been found that materials such as 13X molecular sieve, silica gel, platinum on alumina and alumina itself adsorb significant quantities of benzene at temperatures as high as 427°. The adsorption capacity of 13X molecular sieve (0.632 mmole/g at 91 mm) at these conditions is markedly greater than those of the other adsorbents. With the exception of platinum on alumina, the adsorption is readily reversible and the heats of adsorption are typical of those ordinarily associated with a physical adsorption process. The heats of adsorption of benzene on 13X molecule sieve, silica gel and η-alumina were determined to be 15.5, 9.8 and 6.8 kcal/mole, respectively, in the range of 260–454°. (Author)

P. E. Eberly, Jr., *J. Phys. Chem.*, **65**, 68–72, January 1961.

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262. The Sorption of Water Vapor by Charcoal as Influenced by Surface Oxygen Complexes.
United States. A study of water sorption isotherms on charcoal coated with different amounts of variously disposed chemisorbed oxygen shows that it is the oxygen disposed as CO_2 which enhances the sorption capacity of charcoal and not the rest of the combined oxygen. The area of the hysteresis loop also increases with increase in the amount of this oxygen. An appreciable amount of water, representing about one mole per mole of CO_2, is held so firmly by charcoal that it is not desorbed even on drying to zero humidity. This enhances the hysteresis effect, which, however, persists though to a smaller extent, even on complete elimination of the combined oxygen. (Authors)

B. R. Puri, K. Murari and D. D. Singh, *J. Phys. Chem.*, **65**, 37–39, January 1961.

16 : 11 : 31 : 33 : 37 : 38

Evolution and Absorption of Gases in Electron Tubes. See Abstr. No. 225.

16 : 11 : 18 : 21 : 22 : 47

Electrical Clean-up of Gases in Hot Cathode Discharge Tubes. See Abstr. No. 231.

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Initial Pumping and Recovery of Ionization Gauges. See Abstr. No. 238.

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Some Barium Getter Problems on the Vacuum Tubes. See Abstr. No. 280.

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Use of Zirconium Sintered Getters. See Abstr. No. 281.

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The Ceto Getter—its Chemical Structure and Hydrogen Gettering Properties. See Abstr. No. 282.

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System Design and the Choice of Materials for the "Nimrod" Vacuum System. See Abstr. No. 368.

18. Gaseous Electronics

18 : 22 : 30

263. Cathodic Etching in a Penning Cold Cathode Discharge.
United Kingdom. An apparatus for cathodic etching using a Penning cold cathode discharge is described. One of the twin cathodes is the specimen to be etched whilst the other is made of aluminium. The cathodes are water cooled so that metals of either low melting point or low sputtering rate will not overheat during the cathodic etching. The Penning system is used because the glow discharge can be maintained at a sufficiently low pressure ($\leqslant 1\mu$Hg) for most of the sputtered atoms to escape from the specimen surface and not be returned by collision with gas molecules. The higher sputtering rate attained at low pressure permits etch patterns to be obtained speedily. Several metals, viz. phosphor bronze, copper, pure iron, mild steel, bismuth, cadmium and Telcoseal 5 (an alloy consisting of 25 per cent chromium in iron with additions of manganese and silicon) have been cathodically etched satisfactorily and photomicrographs of some of the etched surfaces prepared. Generally the cathodically etched surfaces were similar to those obtained by chemical etching, but only cathodic etching truly exposed the crystalline structure of Telcoseal 5. (Author)

P. T. Stroud, *Vacuum*, **9**, 269–273, 1959.

18

264. The Measurement of Thermionic Emission in Discharge Tubes.
A new but simple procedure is described for measuring the zero-field emission I_0 in gas-filled discharge devices. Probes are not used. The noise due to the oscillation of positive ions in the potential well adjacent to the cathode is detected and amplified. The current through the device at which the noise drops to a small value is taken to be I_0. The emission of oxide cathodes in fluorescent lamps is found by this technique to increase with increasing pressure of rare gas. The interpretation of this effect is that the rare gas retards the evaporation of barium from the cathode and permits a higher equilibrium concentration of excess barium in the cathode for a given rate of production. The higher the rare gas pressure, the lower the rate of escape of barium from the cathode surface and the higher the concentration of excess barium in the cathode*. (Author)

J. F. Waymouth, *Sylvania Technol.*, **13**, 2–10, January 1960.
*See April 1960 issue of *Sylvania Technologist* for correction on p. 49.

18 : 11 : 16 : 21 : 22 : 47

Electrical Clean-up of Gases in Hot Cathode Discharge Tubes. See Abstr. No. 213.

18 : 33

Vacuum as an Insulator. See Abstr. No. 315.

19. Radiation

19 : 20 : 30 : 56

265. Apparatus for the Controlled Deposition of Optical Film Systems.
United Kingdom. Some of the problems of producing multi-layer interference systems are discussed in relation to the design of the deposition plant and film thickness control apparatus. A vacuum plant is described in which multi-layer films of evaporated or sputtered layers can be deposited in sequence on a rotating plane surface. The thickness of the individual films is controlled by measuring their reflectance or transmittance during deposition with a modulated-beam photometer of high sensitivity and stability. The monitoring light is chopped at frequency of 33 c/s and the output from the photocell amplified by a tuned low frequency amplifier. The conditions for obtaining minimum light scattering in the instrument are discussed. The design of the low frequency amplifier is considered in relation to noise level and filter design. In conclusion the use of the combined apparatus is described for producing a variety of optical systems such as TiO_2 beam-splitters, Bi_2O_3/Au/Bi_2O_3 heat reflecting mirrors, two-layer anti-reflection coatings of Bi_2O_3/MgF_2 and all-dielectric broad-band filters of MgF_2/ZnS. (Authors)

W. Steckelmacher, J. M. Parisot, L. Holland and T. Putner, *Vacuum*, **9**, 171–185, 1959.

19

266. Optical Properties of Sb, Te, and Ti Films in the Vacuum Ultraviolet.
Om P. Rustgi, W. C. Walker and G. L. Weissier, *J. Opt. Soc. Amer.*, **51**, No. 12, 1357–1360, December 1961.

19

267. Concept of Cross-Spectral Purity in Coherence Theory.
L. Mandel, *J. Opt. Soc. Amer.*, **51**, No. 12, 1342–1351, December 1961.

19

268. Attainment of High-Resolution Gratings by Ruling under Interferometric Control.
George W. Stroke, *J. Opt. Soc. Amer.*, **51**, No. 12, 1321–1340, December 1961.

19

269. Fringes of Equal Inclination in the Double-Passed Michelson Interferometer.
P. Hariharan and D. Sen, *J. Opt. Soc. Amer.*, **51**, No. 6, June 1961.

19

270. Color Measurement of Metal Surfaces.
J. M. Williams, *J. Opt. Soc. Amer.*, **51**, No. 6, June 1961.

19 : 33

271. The Attainment of Clean Surfaces by Breaking Crystals in Ultra-High Vacuum.
United Kingdom. Two experiments are described with the object of determining some of the electronic properties of semiconductor surfaces produced by fracture in high vacuum. In one experiment the photoelectric emission is being measured from freshly broken indium antimonide and gallium arsenide, and from cleaved bismuth telluride. The surfaces are produced and the measurements carried out in sealed-off tubes pumped by ionization gauges. The pressures achieved in these tubes are between 10^{-7} and 10^{-9} mmHg. In the other experiment, the transverse mobility of induced surface charge and the photoconductivity are being investigated on germanium surfaces obtained by cleavage in a vacuum of order 10^{-10} mmHg. This vacuum is obtained in a continuously pumped system with a mercury diffusion pump and ionization gauge. Details of the two kinds of tube will be shown. (Authors)

P. C. Banbury, G. A. Barnes, D. Haneman and E. W. J. Mitchell, *Vacuum*, **9**, 126–127, 1959.

19 : 30 : 31

272. Oblique Reflectance and Transmittance Measurements on Aluminium Films.

Syria. Reflectances and transmittances of thin aluminium films deposited on glass were measured as a function of the angle of incidence and the state of polarization of the incident light. The experimental results were compared with theoretical predictions. The oxide layer which forms on the Al film as this is exposed to air was taken into account and discussed. Experimental results indicate that the refractive index of an Al film thicker than 80 A is independent of thickness. (Author)

T. Turbadar, *Vacuum*, **9**, 139–145, 1959.

19 : 30

The Formation of Luminescent Films by Evaporation. See Abstr. No. 303.

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20. Pumping Systems

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273. Semi-Automatic Control of Vacuum Pumping Systems.
N. C. Balchin and B. L. Mordike, *Vacuum*, **9**, 264–268, 1959.

20 : 10 : 11 : 12 : 21

Recent Advances in Ultra-high Vacuum Technology. See Abstr. No. 223.

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Vacuum System for a Thirty Billion Electron Volt Particle Accelerator. See Abstr. No. 232.

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The Production of Ultra-high Vacua by Means of a Diffusion Pump. See Abstr. No. 233.

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The Gas Sorption Characteristics of Penning Pumps and Titanium Films. See Abstr. No. 241.

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21. Pump and Pump Fluids

21 : 22

274. A Partial Pressure Vacuum Gauge working according to the Principle of the Electrical Mass Filter.
Karl-Georg Günther, *Vacuum*, **10**, 293–309, 1960.

21 : 41 : 33

275. Selective Getters.
Czechoslovakia. Studies of the emission stability of oxide cathodes with tungsten core have shown that the presence of hydrogen in the residual atmosphere is of great significance for the stability of the emission properties of the cathode. A number of experiments was therefore carried out in order to ascertain the effect of hydrogen on the work function and the conductivity of the oxide layer with nickel and tungsten support. To obtain practical results we had to increase the partial hydrogen pressure in the bulb which was accomplished by using a getter with selective effect for hydrogen. The above mentioned getter was prepared and its properties in radio-tubes investigated. (Authors)

Ing. J. Hejzlar and Ing. V. Horacek, *Vacuum*, **10**, 231–233, 1960.

21 : 33

276. Noise Reduction in Microwave Tubes by Getter-Ion Pumping.
United Kingdom. The problem of ion noise in microwave oscillators and amplifiers is explained. It is shown that residual gas pressures of approx. 10^{-9} Torr must be maintained in order to eliminate ion noise. A description is given of the construction of an ion getter pump which is built into a backward wave oscillator and designed to operate continuously while the oscillator is in use. The problems associated with maintaining low pressures in microwave vales are discussed. (Author)

N. W. W. Smith, *Vacuum*, **10**, 106–109, 1960.

21 : 33

277. On the Use of Metal-Oil Diffusion Pumps when operating with Discharge Tubes sensitive to Hydrocarbons.
Liechtenstein. In the stationary state the ultimate pressure in the recipient over a metal-oil diffusion pump having metal seals is defined, as well known, by the sum of the saturation vapour pressure of the oil and of the partial pressures of the thermal decomposition products (10^{-8} Torr equivalent N_2 pressure = 10^{-9} Torr true pressure). When operating with tubes sensitive to hydrocarbons it is however often desirable to attain even lower pressures. This is possible even without the use of deep cooling or Alpert traps by operating in a non-stationary state, i.e. immediately after the heating up of the valves. For the duration of the non-stationary state and for the magnitude of the pressure attainable in this state the adsorption characteristics of the oil molecules and the dimensions of the vacuum conduits are decisive. By the aid of a field electron microscope it has been proved that it is possible even with vacuum systems capable of being dismantled and provided with metal-oil diffusion pumps to attain completely clean surfaces, which in particular are free from oil molecules, and to keep them so over long periods. Consequences thereof for technological application have been pointed out. (Author)

R. A. Haefer, *Vacuum*, **10**, 118–120, 1960.

21 : 33

278. On the Use of Getters in TV Cathode-ray Tubes.
France. Since some years, to increase the pictures brightness, the Kinescopes have been aluminized. But the unavoidable heavy aluminium thickness in the centre of the screen is visible, as dark centre, at low ultor voltage. For this reason, the minimum operating voltage is indicated on each type data. It is however easy for the Kinescopes manufacturer to remain in the allowed limits taking account that the Getter Baryum layer, which has a higher atomic mass, is more opacious than the aluminium film and can increase the defect occasioned by the bad uniformity of this one, affecting the colour uniformity of the screen at low ultor voltage. It appears convenient to direct, during the getter flash the Baryum molecules, in order to see they deposit out of the screen area. A good solution has been found by the S.A.E.S. who supply a ring getter with very efficient deflector. The rational use of this getter introduces special cautions, otherwise the new getter type will be worse than the old one. During this communication, some test results will be given illustrating perfectly this theory. (Author)

Elie Biolley, *Vacuum*, **10**, 151–152, 1960.

21 : 33

279. Clean Up of Gases in TV Picture Tubes by Barium Getters.
Japan. In this brief communication the authors present the comparative results obtained in television tubes where getters of Japanese and Italian production have been used. The measurements are carried out using the electron gun of the tube as an ionization gauge and applying the well known " gas ratio " technique normally used for pressure measurements in picture tubes. The various types of gases employed are introduced into the tube by breaking an ampoule containing a known quantity of the gas in question, which has been placed within the tube prior to its sealing. Data are given about the influence of the various gases employed on the emission from the cathode, as well as on the behaviour of the barium film after sorption of the different gases. (Authors)

Hisao Takayama and Hideki Bobayashi, *Vacuum*, **10**, 153–155, 1960.

21 : 33 : 16

280. Some Barium Getter Problems on the Vaccum Tubes.
Japan. The writers have carried out experiments on the action

and behaviour of getters as used in the actual production of, for example, receiving tubes, power tubes, cathode ray tubes, mercury rectifiers and X-ray tubes. Initially the results obtained from the study of the flashing conditions of the getter and the effect of these conditions on the sorption of gases are presented. Results are given for the quantity of the gas sorbed during the first minute, the following four minutes and the successive 10 min, for getters which have been evaporated for 10 and 60 sec. The difference in the quantity of gas initially sorbed when using different times of flashing are quite remarkable in the case of N_2 and H_2. Due to this the quantity of gas sorbed can nearly be doubled by a rapid firing of the getter. This difference is less marked for O_2 and negligibly small for CO and CO_2. Similar studies have been made using rare gases; these studies have been helped by using the electron microscope to study the surface of the getter film. Studies have also been made on the influence of the distance between getter and condensing wall and hence of the condensing area of barium film. By examining cathode ray tubes, the dependance of the tube pressure and life on the conditions of flashing of the getter have been studied. In non aluminized picture tubes data are presented giving the most favourable angle of connection of the getter assembly to the electron gun. The modifications made to the cathode structure of X-ray tubes in order to obtain the most favourable conditions when using the getter are reported. Data on the pressure obtained under such circumstances are also presented. Subsequently a study is given of the gas sorption by barium, magnesium and titanium, in mercury vapour tubes. Finally there is a study of the influence of the getter on the emission from the oxide cathodes employed in mercury rectifiers made with an apposite apparatus. (Author)

Kazuji Hashimoto and Kenji Kitagawa, *Vacuum*, **10**, 156–161, 1960.

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281. Use of Zirconium Sintered Getters.

France. The statement concerns the general conditions of elaboration and some examples of application of a getter obtained by sintering of a mixture of powders of zirconium hydride (80 per cent in weight) and of aluminium (20 per cent in weight). The getter holder (preferably in a circular form) is made of nickel pressed or of molybdenum embossed. A cold compression of the powder directly on its holder is proceeded. The sintering operation is made under high vacuum at about 1050°C. Some tests of application of those getters have been made with HT tubes EY81 and 6AX2N, and with the 21B6 and 5725 tubes. The results are very good after 500 hr life. Tests made with power valves of 12 kW with graphite anode (type 3T12000A5) with getters of large dimensions, show that the output was now in good condition during working. In general meaning, the getter being not volatilized, but only heated at high temperature, we do not observe metallic settling on the inner surface of the bulbs so that risks of leakage on cold inner surface or of noxious capacitances reduce considerably. We notice a very steady work. (Author)

J. M. Sourdillon, *Vacuum*, **10**, 162–165, 1960.

21 : 16 : 33

282. The Ceto Getter—its Chemical Structure and Hydrogen Gettering Properties.

Netherlands. Ceto, which is an alloy of thorium, mischmetall and aluminium is used as a non-evaporating getter. In the course of an elaborate investigation of the ternary system Th–Ce–Al, it has been proved that its crystallographic structure is of the $CuAl_2$ type, just like the closely related binary compound Th_2Al. The properties of the Th_2Al, Ceto and intermediate compounds with regard to hydrogen were studied. X-ray and neutron diffraction, supplemented by nuclear magnetic resonance measurements, each at liquid nitrogen temperature, and room temperature, gave information about the structure of the reaction products. Hydrogen equilibrium-pressure measurements at temperatures from 250°C up to 700°C gave thermodynamic information and enabled to calculate the equilibrium pressures at lower temperatures. A kinetic study, based on a simple model, of an autocatalytic sorption is reported. (Author)

J. H. N. van Vucht, *Vacuum*, **10**, 170–177, 1960.

21 : 41

283. Structure of Barium Getter Films.

Netherlands. The structure of barium getter films, made by means of barium aluminium alloy getters, has proved to be of granular nature. A hypothesis is advanced in which it is stated that, during the heat treatment of a getter, barium mainly will be sputtered instead of evaporated. Various facts to support this hypothesis will be discussed. (Author)

H. J. R. Perdijk, *Vacuum*, **10**, 204–209, 1960.

21 : 33 : 41

284. Study of the Surface Structure of Barium Getter Deposited Film by an Electron Microscope.

Japan. The rate of gas sorption of the flash-getter depends especially on whether the structure of the deposited film is in an amorphous state or not. Therefore, if we observe the surface structure of the deposited film and also measure the saturated value of sorption or electrical resistivity of the deposited film, this may help to clarify the mechanism of sorption and develop an interesting method to study getters. The preparation of specimens suitable for the electron microscope and some of the results obtained are described. (Author)

K. M. Yazawa, *Vacuum*, **10**, 210–211, 1960.

21 : 32

285. Evapor-ion Pump Development at the University of Wisconsin.

United States. Evapor-ions pump have been developed at the University of Wisconsin for a variety of applications. The largest of these pumps has a diameter of 24 in. It is used in connection with a hydrogen negative ion source and gives a pumping speed for hydrogen of approximately 15,000 l/sec at pressures in the region of 5×10^{-6} mmHg. Several pumps of 12 in. diam. and of 8 in. diam. are now being used. For other applications pumps of 1 in. diam. and 2 in. diam. have been developed. Evaporation techniques, starting techniques, and general operational characteristics of these pumps will be given. (Author)

R. G. Herb, *Vacuum*, **9**, 97–107, 1959.

21

286. Evaluating a Getter-Ion Pump for Vacuum Firing Furnace Applications.

Tests were made to determine the effectiveness of a getter-ion pump for use in the vacuum firing of tube parts. Using a 55-liter furnace and a 250 liter/sec VacIon pump, the speed was equal to or slightly better than that of a conventional 4 inch oil-diffusion pump operating in the 10^{-5} mmHg pressure range. The final vacuum obtained with the getter-ion pump was more than one decade higher than that obtained with the MCF-300 diffusion pump with liquid-nitrogen trapping on a static test. The former could be flooded when evacuating an oil-contaminated furnace operating at 1100°C for an extended time. (Author)

R. T. McKenzie, *Sylvania Technol.*, **13**, 50–51, April 1960.

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22. Gauges

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287. Improvement in Operation with McLeod Gauge.
N. A. Florescu, *Vacuum*, **10**, 329–330, 1960.

22 : 37
288. Calibration Factors of Ionization Gauges for Hydrocarbon Gas Mixtures.
L. Elsworth, *Vacuum*, **10**, 266–267, 1960.

22
289. A Tetrode Ionization Gauge.
P. Schwerdtfeger, *Vacuum*, **10**, 330–331, 1960.

22 : 21
290. A Precision McLeod Gage for Volumetric Gas Measurement.
United States. The modified McLeod Gage desicrbed is designed to measure pressures between 10^{-3} and 10^{-4} Torr with an accuracy of $\pm$ 2 per cent. A large-bore side arm isolated from the gage by a cut-off replaces the usual open-end capillary. This feature provides the means for calibrating the variations in capillary depression of mercury at every position along the length of the remaining capillary without contributing to the volume of the gage. A tapered plug used to seal the capillary end eliminates sticking even at 10^{-7} Torr and also extends the range of stable calibration in the ground capillary bore up to the end seal, thus extending the usefulness of the gage to a lower pressure limit. With these innovations, a gage of 200 ml capacity with a capillary of one-half mm bore was found adequate for the accuracy sought. Solution of helium in the pyrex capillary accounts for errors estimated between 1 and 3 per cent ; hence for volumetric calibration neon is preferable to helium.
(Authors)
H. H. Podgurski and F. N. Davis, *Vacuum*, **10**, 377–381, 1960.

22 : 12 : 31 : 33 : 38 : 37
291. The Applicability of the Omegatron to Continuous Analysis of Residual Gases.
United Kingdom. An experimental study is described in which

residual gases were analysed by means of a cyclotron resonance mass spectrometer of the omegatron type. Analysis was continuous before, during and after both (a) ion pumping with a Bayard–Alpert pattern hot-cathode gauge and (b) the dispersal of a barium getter. Results are more extensive than any published hitherto and are presented both as mass spectra and the variation of gas constitution with time throughout each stage of the above operations. The study illustrates the potentialities of the omegatron as a tool for solving many problems existing in vacuum technology. In particular, by regarding the Bayard–Alpert pattern gauge as an electron tube, it is shown that the omegatron is well suited to the analysis of residual gases during the manufacture and life of tubes. (Authors)

Franklin A. Baker and Tiziano A. Giorgi, *Vacuum*, **10**, 58–63, 1960.

22 : 41

292. Some Results of the Measurement of Caesium Vapour Pressure in Photoelectric Tubes during their Manufacture and Life.
Yugoslavia. Residual caesium pressure (P_{Cs}) in phototubes with Ag–O–Cs and Cs_3Sb cathodes have been determined by using the method described in the previous paper and compared to the calculated values. P_{Cs} in a Cs_3Sb cell at room temperature is about 10^{-14} Torr, and in a Ag–O–Cs cell about a hundred times lower. We observed an appreciable increasing of P_{Cs} in Cs_3Sb photo-cells during the operation. "Current activation" of Cs_3Sb photocathodes can be explained by this effect. P_{Cs} data for different photocathode activation processes of photocells and photo-multipliers are given. Sensibilization of photocathodes with minute quantities of oxygen lowers the P_{Cs}. Relations between P_{Cs} and photomultiplier dark current are discussed. (Authors)

E. Kansky and S. Jerič, *Vacuum*, **10**, 240–244, 1960.

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293. Double Pirani Bridge Leak Detector.
G. Calvi, *Vacuum*, **10**, 64–67, 1960.

22 : 27 : 37

294. Measurements on the Properties of a Simple Omegatron.
United Kingdom. Measurements have been made on a simple omegatron mass spectrometer, to show the effect of various parameters on the sensitivity, resonant frequency, resolution and background ion current. Increase of magnetic field has been shown to cause a marked improvement in peak-to-background ratio, and to improve resolution approximately as predicted by the simple theory. The range has been extended to include Hg, the height of Hg peaks having been shown to be proportional to the pressure of Hg vapour present. Using the results it has been possible to make a practical appraisal of the sensitivity of the omegatron as a leak detector. This leads to less optimistic sensitivity values than have been quoted on theoretical grounds. (Author)

D. S. Stark, *Vacuum*, **9**, 288–294, 1959.

22

295. A Piezoelectric Oscillator Manometer.
United Kingdom. This paper describes a simple manometer for the measurement of pressures of gases and vapours within the range 760 Torr to 10^{-1} Torr, with a linear scale. It uses the damping effect of the gas or vapour upon the sustained vibrations of a commercially available piezoelectric quartz crystal. The damping effect is examined theoretically and the behaviour of the gauge is shown to be generally in accordance with calculation. (Author)

D. J. Pacey, *Vacuum*, **9**, 261–263, 1959.

22 : 21 : 33 : 37 : 47

296. Experience in Using Mass-Spectrometric Methods in Electro-Vacuum Technology.
I. A. Kaljabina and Ya. A. Yukhvidin, *Vacuum*, **9**, 117–125, 1959.

22

297. Mass Dependent Ion Collection Efficiencies in a Mass Spectrometer.
Note by D. A. Kubose and W. H. Hamill, *J. Phys. Chem.*, **65**, 183–184, January 1961.

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Analysis of Partial Pressures by Means of Omegatron and Farvitron. See Abstr. No. 226.

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Measurement of Gas Evolution and Absorption from Materials used in Vacuum Tubes. See Abstr. No. 367.

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298. A Simple Flexible Vacuum Joint.
P. I. P. Kalmus, *Vacuum*, **9**, 147, 1959.

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299. Experience in Designing and Manufacturing All-Metal Vacuum Systems.
M. L. Lyubimov, K. P. Shakhov and Ya. A. Yukhvidin, *Vacuum*, **9**, 108–115, 1959.

24. Valves

24 : 11 : 21 : 25 : 32

High-Vacuum Pumps and Units for Accelerators. See Abstr. No. 230.

24 : 23 : 25 : 41

Experience in Designing and Manufacturing All-Metal Vacuum Systems. See Abstr. No. 299.

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Carbon Contamination of Glassware used for Vacuum Purposes. See Abstr. No. 316.

25. Baffles, Traps, and Refrigeration Equipment

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High-Vacuum Pumps and Units for Accelerators. See Abstr. No. 230.

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The Production of Ultra-High Vacua by Means of a Diffusion Pump. See Abstr. No. 233.

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Experience in Designing and Manufacturing All-Metal Vacuum Systems. See Abstr. No. 299.

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Vacuum Techniques and Components used for a Continuously Pumped Linear Electron Accelerator. See Abstr. No. 312.

26. Automotive Protection and Control Equipment

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300. A Shutter for Use Between Source and Work During Vacuum Evaporations.
W. R. Lamb, F. A. Rhoads and P. S. Applebaum, *Vacuum*, **9**, 147–148, 1959.

26

301. Automatic Level Control for Liquid Nitrogen Trap.
L. D. Miller and P. N. Petersen, *Vacuum*, **9**, 231–232, 1959.

26 : 20

Semi-Automatic Control of Vacuum Pumping Systems. See Abstr. No. 273.

26 : 21 : 25 : 32

Vacuum Techniques and Components used for a Continuously Pumped Linear Electron Accelerator. See Abstr. No. 312.

27. Leak Detectors and Leak Detection

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Measurements on the Properties of a Simple Omegatron. See Abstr. No. 294.

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30. Evaporation and Sputtering

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302. A Pumping Schedule for a Power Travelling Wave Tube.
J. R. Tew, *Vacuum*, **10**, 110–111, 1960.

30 : 19

303. The Formation of Luminescent Films by Evaporation.
S. K. Bateman, *Vacuum*, **10**, 329, 1960.

30 : 37 : 56

304. Vacuum Deposition of Dielectric Films for Capacitors.
United Kingdom. The first part of this work deals with the evaporation of inorganic materials suitable for making thin dielectric layers for capacitors. The evaporation of a mixture of oxides, for example a glass, is also discussed, and the electrical properties of some glasses are given. The stability of metal oxide compounds at high temperatures is considered in relation to their free energies of formation. The reported vapour pressures of the components of the more commonly used glasses show that their evaporation is not possible from a single vapour source without separation of the components by fractional distillation. The second part of the report describes an experimental investigation into the preparation and properties of dielectric films of silicon oxide in the thickness range 0.14 to 1.7μ produced by the evaporation of silicon monoxide at varying rates. Capacitors of 0.001–0.01μF/cm^2 have been deposited on " Pyrex " glass using evaporated aluminium films for the conducting-plates, and measurements of the electrical properties of the silicon oxide films have been made. The working voltage of capacitors in this range lies between about 12 and 60 V depending upon the thickness of the dielecrtic and upon the working temperature. At temperatures above 200°C the values of loss angle and leakage current are generally unacceptable. It is established that the rate of deposition of the oxide layer has a marked effect on the loss angle, dielectric constant and leakage current. Generally the lowest values of leakage current and loss angle are obtained with rates of deposition below 5 Å/sec. The dielectric constant of slowly deposited silicon oxide films is less than that of bulk silica, which is attributed partly to their lower density. The work carried out with silicon oxide shows that satisfactory dielectric films for capacitors can be made by the evaporation technique. (Author)

G. Siddall, *Vacuum*, **9**, 274–287, 1959.

30 : 41

305. Adhesion of Evaporated Metal Films.
United States. An abrasion-resistivity test was developed to study the adhesion of vacuum-deposited aluminum films on glass surfaces. The test consists of measuring the electrical resistance of the metal film during abrasion by a stream of fine silicon carbide particles. An analysis is given of the anticipated test results on homogeneous and nonhomogeneous metal films and on effects near the interface. Differences in the plating and annealing conditions of evaporated aluminum films were detected by the abrasion-resistivity test. Poorest adhesion was found on platings made on unclean surfaces and platings made at a slow rate of evaporation of the metal. The optimum substrate temperature for good adhesion was determined to be 175°C. Annealing of the aluminum film resulted in formation of a surface oxide layer and development of an interlayer compound at the interface. (Authors)

F. Schossberger and K. D. Franson, *Vacuum*, **9**, 28–25, 1959.

30 : 33 : 41

306. A Thin Film Resistor for Measuring Strain.
United Kingdom. An investigation has been made into the measurement of mechanical strain in terms of the electrical resistance changes induced in an evaporated metal film on a flexible support cemented to a stressed surface. The results show that a polyester foil coated with a nickel-chromium alloy is suitable for short-term measurement purposes. (Authors)

G. Siddall and G. Smith, *Vacuum*, **9**, 144–146, 1959.

30 : 41

307. The Structure and Density of Iron Films formed by Thermal Evaporation.
United Kingdom. The densities have been determined of iron films of thickness 800–1600 Å deposited on the cleavage faces of rocksalt crystals maintained at 470°C. The films are monocrystalline, as shown by electron diffraction, and appear continuous when examined in the electron microscope. The values obtained for the densities are found not to differ significantly from that for the bulk metal. (Authors)

O. S. Heavens, M. M. Brown and V. Hinton, *Vacuum*, **9**, 17–20, 1959.

30

308. The Adhesion of Vapor-Deposited Molybdenum Coatings.
These coatings were produced by reduction of molybdenum pentachloride with hydrogen at a pressure of 20 Torr and a temperature of 900°C. The thickness of the deposits produced on various metallic substrates ranged from 2 to 28 mils. The degree of adherence was evaluated by visual inspection of the coating after partial and complete flattening of the $\frac{1}{2}$-in. diameter tubes on the inside of which the molybdenum was deposited. Microsections were also made. The most important variables which affected the adherence were (1) purity of raw materials, (2) sample preparation, (3) chemical composition of the substrate. The presence of oxychlorides in the plating system, which were subsequently reduced to produce layers of MoO_2 in the plate, destroyed any adherence, even if the oxide films were less than 0.1 mil thick. Pure iron, stainless steel, low-carbon steel, and chrome-plated iron or steel showed very poor adherence of the molybdenum coating. Pure copper, nickel, Inconel, or any of the iron or steel samples which had first been electroplated with nickel, copper, cobalt, or thodium exhibited excellent adherence. It is concluded that adherent coatings of molybdenum can be vapor plated onto surfaces which are free of carbon or constituents that form more stable chlorides than molybdenum.

S. T. Vlodek and J. Wulff, *J. Electrochem. Soc.*, **107**, 565–568, June 1960.

30 : 41 : 16 : 21

Carbon Monoxide Sorption by Barium Films. See Abstr. No. 250.

30 : 16 : 21 : 33 : 41

Nitrogen Sorption by Barium Films. See Abstr. No. 251.

30 : 18 : 22

Cathodic Etching in a Penning Cold Cathode Discharge. See Abstr. No. 263.

30 : 19 : 20 : 56

Apparatus for the Controlled Deposition of Optical Film Systems. See Abstr. No. 265.

30 : 19 : 31

Oblique Reflectance and Transmittance Measurements on Aluminium Films. See Abstr. No. 272.

30 : 26

Automatic Protective and Control Equipment. See Abstr. No. 300.

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31. Evacuation and Sealing

31 : 37 : 22

309. Residual Gases in Picture Tubes.

Netherlands. The omegatron, a small mass spectrometer, has been used to analyse the residual gas in television picture tubes. First the principle of operation of the omegatron is briefly recalled, and a short description of the Philips execution is given. This instrument is mounted in a side arm connected to the bulb of a television tube, together with an ionization gauge and the whole assembly is pumped simultaneously. Both completed tubes and partly processed bulbs have been prepared in this way. The residual gas after seal-off has been analysed at different stages of processing, i.e. before and after flashing the getter, after drawing current with the ionization gauge and during shelf-life. The gas content after seal-off mainly consists of hydrogen, nitrogen and methane. Generally in the bulb blanks hydrogen is the main gas whereas in completed tubes nitrogen has the higher pressure. In all cases small traces of H_2O, CO and CO_2 have been found. All these gases disappear almost completely after the getter has been flashed, but this operation produces an appreciable amount of hydrocarbons and some argon. Drawing current with the ionization gauge or with the electron gun of a completed tube results in a breakdown and a subsequent adsorption of the hydrocarbons. On shelf-life these gases are partly desorbed. Scanning the screens results in a very rapid decrease in pressure of the hydrocarbons. (Authors)

J. C. Francken and J. van der Waal, *Vacuum*, **10**, 22–27, 1960.

31 : 33 : 22

310. Emploi d'une Diode d'Essais comme Moyen de Contrôle des Matériaux de Construction des Tubes Électroniques.

France. Experience in the manufacture of high power microwave tubes (multi-MW range) has shown that the materials which constitute the tube are as much important as the materials which constitute the thermionic cathode itself. Indeed, where the oxide coated cathode is concerned, it has been recognized since the time of Wehnelt that the residual gas and the cathode performance are related. For a long time, the influence of the gas evolved of the electrodes and the tube envelope during operation, on cathode emission, has been recognized, too. All these phenomena have been designated " ambient phenomena " where " ambient " means the gases or vapours in the vicinity of the cathode and, in a wider sense, the sources of these gases and vapours which present the constructional parts of the tube. Since in the tube practice it is not always convenient to point out the nature of the ambient gases in function of the materials and the treatments they undergo, it has been found useful to examine the influence of the materials on an oxide coated cathode in a test diode, a technique which is in principle well known for controlling the cathode and tube materials of receiving tubes (" standard diodes "). The diode in question is adapted to the needs of pulsed tubes and allows—thanks to this fact and contrary to the usual standard diodes—to measure the cathode performance under the operating conditions except the anode voltage which is lowered. After a rapid description of this diode, it is shown that the influence of the ambients reveals three different behaviours of a $I^{2}/^{3}$ plot, where the available useful current (under space charge limitation) is limited either by apparition of the sparking phenomenon or by saturation. The influence of the operating conditions (d.c. or pulsed operation, pulse length, repetition frequency) on the current where the sparking occurs are demonstrated and the results obtained with certain anode materials are indicated; that is: Iron, Kovar, Titanium, Molybdenum, Copper, Platinum and Nickel. The best anode materials were platinum and nickel; in this latter case, in pulsed operation a current density of more than 100 A/cm² has been obtained, the limitation occurring not by saturation, but by sparking. Finally, the influence of the glass used as the diode envelope is shown. In conclusion, the diode reveals as a relatively simple control device. Nevertheless, when the nature of the ambients must be pointed out, more improved devices should be applied, such as the mass-spectrometer, a subject of the next paper. (Author)

J. P. Freytag, *Vacuum*, **10**, 40–48, 1960.

31 : 33 : 22 : 12

311. An Electrostatic Mass Spectroscope.

Germany. During the last few years, several methods have been known to analyse the residual gas of high vacuum devices by means of small mass spectrometer tubes. In these tubes which have a resolving power of about 20 or 30, the principle of mass separation by different times of flight is employed. Unfortunately, at pressure below 10^{-6} Torr, the signal currents generated by these tubes are so small that for the registration of the whole mass spectrum a comparably long time is required. In order to avoid this drawback a new mass spectrometer tube has been developed. Due to the high signal-output of this tube the whole mass spectrum, ranging from H^{+} up to Hg^{+}, can be displayed on an oscilloscope at 50 Hz. Therefore, a practically continuous control of the residual gas can be achieved. The signal of the mass spectrometer tube is generated by a cloud of charged particles of equal relative masses which oscillates along the axis of an electrostatic field with axial symmetry. This ion cloud consists of numerous superposed elementary clouds each of which being created by an electron beam in a strong accelerating field near one end of the tube. An electrode on the other end of the tube is used to pick up the displacement-current induced by the ion cloud. The ionizing electron beam is intensity-modulated with a variable frequency. Therefore, an ion cloud is built up only when the variable modulation frequency of the beam coincides with the oscillation frequency of any sort of ions. At frequencies other than those of the ions present in the residual gas, the elementary ion clouds cannot form one big cloud because practically no phase relation between them exists. The space-charge action of the elementary clouds explains that the functional dependence between mass intensity and partial pressure is not linear. A special tube having a resolving power $m/\triangle m \approx 20$ at all masses, is described which can be used at pressures below 5×10^{-5} Torr. This upper limit is set by the mean free path of the ions. The lower limit depends on the shot noise of the first amplifier stage. Thus, at a registration speed of 50 Hz, partial pressures in the order of 10^{-8} Torr can be detected. At still lower pressures a second operation method should be adopted which even permits the use of an electron multiplier. (Author)

Werner Tretner, *Vacuum*, **10**, 31–34, 1960.

31 : 21 : 25 : 26 : 32

312. Vacuum Techniques and Components used for a Continuously Pumped Linear Electron Accelerator.

United States. A vacuum system has been designed to continuously pump a linear electron accelerator having an internal volume of approximately 30 l. and produce vacuums down to 1×10^{-8} or better. The construction avoids all organic materials and is capable of being baked out at 450°C ; design details of flanges, envelope construction, insulators and valves are discussed. Performance of the diffusion pump traps, which require no refrigeration, and their construction are described. Operating characteristics of the over-all system are discussed in terms of accelerator performance. (Author)

R. C. Marker, *Vacuum*, **9**, 128–133, 1959.

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Residual Gas Pressure in Electron Tubes. See Abstr. No. 229.

32. Nucleonics

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Vacuum System for a Thirty Billion Electron Volt Particle Accelerator. See Abstr. No. 232.

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Evapor-ion Pump Development at the University of Wisconsin. See Abstr. No. 285.

32 : 31 : 21 : 25 : 26

Vacuum Techniques and Components used for a Continuously Pumped Linear Electron Accelerator. See Abstr. No. 312.

33. General Physics and Electronics

33 : 41 : 37

313. Application de la Technique du Vide à la Fabrication des Transistors.

H. Bumm et O. Korn, *Vacuum*, **10**, 424–481, 1960.

33 : 22

314. Ion Movements in an Omegatron.

Germany. The motion of resonant and nonresonant ions in the omegatron, already described in the preceding paper of A. Klopfer and W. Schmidt, is investigated. It is demonstrated that the auxiliary electrostatic field in this type of omegatron creates conditions which make for optimum collection of the resonant ions and insure consistent reproducibility. Space-charge effects are estimated, and an expression is derived for the resolving power. (Author)

G. Schuchhard, *Vacuum*, **10**, 373–376, 1960.

33 : 18

315. Vacuum as an Insulator.

United Kingdom. This article reviews the properties of vacuum when it behaves as an electrical insulator, the factors which determine breakdown, and the hypotheses advanced to account for the breakdown. Conclusions are drawn which suggest the direction which future developments might take. (Author)

R. Hawley, *Vacuum*, **10**, 310–318, 1960.

33 : 24

316. Carbon Contamination of Glassware used for Vacuum Purposes.

United Kingdom. The report deals with the detection, elimination, and some properties of a film of carbonaceous matter which exists on glass pinches and envelopes as used in normal receiving valves. The film is resistant to conventional washing methods, and probably originates either from lubricating oil used on glass forming machines or from the cathode binder. It is indirectly identified by the deposition of a layer of carbon on the surface of the oxide cathode resulting from heating the glass envelope at a certain stage in the vacuum processing of the valve. Some effects on valve performance resulting from this form of contamination are implied, and some methods by means of which the film can be eliminated are described. (Author)

H. Batey, *Vacuum*, **10**, 263–265, 1960.

33 : 21

317. Electron Tube Processing with Getter-Ion Pumps.

United States. A description of the VacIon® getter-ion pump and of its physical processes is presented. Its performance and advantages over older pumping techniques are discussed. Particular attention is paid to the processing of electron tubes with VacIon pumps. Actual experience with thousands of tubes is presented, pointing out the very considerable benefits as regards performance and economic savings achieved by employing this technique. Brief mention is made of two other matters: (1) The use of sorption pumps to go from atmospheric pressure to the starting region of VacIon pumps. This completely eliminates the possibility of introducing contaminants into a system during processing. (2) The use of VacIon pumps as appendages of electron tubes so as to maintain the vacuum against the consequences of 1—inadequate processing, 2—outgassing during operation, and 3—leaks. (Authors)

L. Malter and H. Mandoli, *Vacuum*, **10**, 121–127, 1960.

33 : 42 : 46

318. Design Approaches for Electron Devices Operating in Critical Environments, Especially Ceramic-envelope Tubes for High-temperature Operation.

United States. On the basis of several surveys conducted for the Armed Services and in the light of current trends in the industry, a review is presented of developments aiming toward reliable components for operation in critical environments where temperatures of the order of 500°C, high shock and vibration levels, and nuclear flux densities are encountered. The construction of high-vacuum tubes for such service presents unique problems of which many have been overcome in recent years. The different design approaches will be briefly described and illustrated, and still existing limitations pointed out. (Author)

W. H. Kohl, *Vacuum*, **9**, 58–62, 1959.

33 : 21

319. An Omegatron Spectrometer, its Characteristics and Application.

United States. The development of an omegatron mass spectrometer as a relatively inexpensive and automatic scanning analyser is described. Operating characteristics of the device in the pressure range 10^{-5} to 10^{-9} Torr are given. Areas of application in which the omegatron is especially suitable are indicated by some preliminary work. (Authors)

E. J. Zdanuk, R. Bierig, L. G. Rubin and S. P. Wolsky, *Vacuum*, **10**, 382–389, 1960.

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The Investigation of Residual Gases in Vacuum Systems. See Abstr. No. 224.

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Residual Gas Pressure in Electron Tubes. See Abstr. 229.

36. Drying, Degassing and Concentration

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320. An Ampoule Freeze-Dryer for Microbiological Research.
Australia. The construction and operation of an ampoule freeze-dryer for drying suspensions of micro-organisms in 72 tubes at controlled temperatures in the range −50 to 20°C are described. In the apparatus the suspensions can be frozen *in situ* by placing the tube holder in thermal contact with the condenser. Means of obtaining reasonably uniform temperatures in different suspending fluids in the same experiment, and of maintaining constant low temperatures in slow drying suspensions are discussed. (Authors)

J. D. Mellor and D. F. Ohye, *Vacuum*, **10**, 245–249, 1960.

36 : 42

321. The Breakage of Glass Ampoules during Freeze-drying.
United Kingdom. It is shown that the nature of the material (its eutectic point and the concentration of the eutectic mixture), the quantity of material in each ampoule and adhesion of frozen material to the glass wall play important roles in causing breakage of glass ampoules during centrifugal evaporative freezing. Other factors are also discussed. (Authors)

N. S. Verma and T. W. G. Rowe, *Vacuum*, **9**, 21–27, 1959.

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37. Metallurgy, Inorganic Chemistry, Analytical Chemistry

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322. Some Practical Examples of the Use of Vacuum in Non-ferrous Metallurgy.
B. Tougarinoff, *Vacuum*, **10**, 466–473, 1960.

37 : 22

323. An Omegraton Mass Spectrometer and its Characteristics. An omegatron with noble-metal electrodes is described, which can be given a constant sensitivity to within 10 per cent by the application of a suitable electrostatic field. The sensitivity is not even affected by the action of corrosive gases and vapours, such as H_2O, CO_2 and CH_4, over long periods, and is reproducible from omegatron to omegatron as long as the dimensions are kept constant. A comparison of the ionization probability given in the literature with that calculated from the calibration curve of the omegatron shows that nearly all the resonance ions formed by the electron beam reach the ion collector. The adjustment of the operating data, needed to achieve this condition is in general independent of the mass. Some characteristics of the omegatron are described. (Authors)

A. Klopfer and W. Schmidt, *Vacuum*, **10**, 363–372, 1960.

37 : 41 : 43

324. Vacuum Treatment of Molten Steel—a New Way of Improving Converter Steel Production.
A. M. Samarin and L. M. Novik, *Vacuum*, **9**, 134–138, 1959.

37

325. Purification of Tantalum Obtained by Vacuum Arc Melting. The purest commercially available tantalum powder was consolidated by a single, vacuum, consumable-arc melting operation yielding ingots of considerably higher purity than the original powder. Interstitial and metallic impurity analyses are presented for a large number of heats made under consistent conditions of ingot and electrode size, arc current, and furnace pressure. The effect of carbon addition to an oxygen-rich starting material was investigated, and the optimum carbon–oxygen ratio for maximum refinement has been located approximately. Under favorable conditions, the oxygen content is reduced by approximately one order of magnitude. (Author)

M. L. Torti, *J. Electrochem. Soc.*, **107**, 33–35, January 1960.

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326. Production Eyes New Furnace for Vacuum Heat Treating.
Article by Anon., *Iron Age*, **187**, 84–85, January 19, 1961.

37

327. New Vacuum Melt Furnace Starts Up.
Note by Anon., *Iron Age*, **187**, 47, January 26, 1961.

37

328. New Vacuum Process for Heat Treating Tool Steels.
Note by Anon., *Metal Progress*, **80**, 7–8, July 1961.

37

329. Large Electron-Beam Furnace Refines Refractory Metals.
Note by Anon., *Metal Progress*, **80**, 9–10, August 1961.

37

330. Zircaloy-2 is Vacuum Hot Pressed.
Note by Anon., *Materials in Design Engineering*, **54**, 15, July 1961.

37

331. Vacuum-Degassed Steel.
Note by Anon., *Mechanical Engineering*, **83**, 60, August 1961.

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332. Elastic and Inelastic Scattering of Low-Velocity H^+ and H_2^+ in Hydrogen.
Article by W. H. Cramer, *J. Chem. Phys.*, **35**, 836–838, September 1961.

40

333. General Theory of Monolayer Physical Adsorption on Solids.
Article by William A. Steele and Marvin Ross, *J. Chem. Phys.*, **35**, 850–862, September 1961.

334. Monolayer Adsorption of Helium on Argon. 40
Article by Marvin Ross and William A. Steele, *J. Chem. Phys.*, **35**, 862–871, September 1961.

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335. Multilayer Adsorption of Helium on Argon.
Article by Marvin Ross and William A. Steele, *J. Chem. Phys.*, **35**, 871–882, September 1961.

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336. Vapor Pressures of the Inert Gases.
Article by Charles E. Hamrin, Jr. and George Thodos, *J. Chem. Phys.*, **35**, 899–902, September 1961.

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337. Vapor Pressures of the Neon Isotopes.
Article by Jacob Bigeleisen and Etienne Roth, *J. Chem. Phys.*, **35**, 68–77, July 1961.

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338. Double and Triple Ionization in Molecules Induced by Electron Impact.
Article by F. H. Dorman and J. D. Morrison, *J. Chem. Phys.*, **35**, 575–581, August 1961.

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339. Interaction of Rare Gases with Semiconductor Surfaces.
Article by Mino Green and Ruth Seiwatz, *J. Chem. Phys.*, **35**, 915–921, September 1961.

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340. On the Classical Boltzmann Equation for Gases.
Article by Frank C. Andrews, *J. Chem. Phys.*, **35**, 922–924, September 1961.

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341. Excitation and Negative Ions in H_2O.
Article by G. J. Schulz, *J. Chem. Phys.*, **33**, 1661–1665, December 1960.

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342. Velocity Analysis of Molecular Beams Generated from NaOH Vapors.
Article by V. S. Rao and Richard S. Schoonmaker, *J. Chem. Phys.*, **33**, 1718–1720, December 1960.

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343. Mass Spectrometric Determination of the Dissociation Energies of the Molecules AgAu, AgCu, and AuCu.
Article by Marcel Ackerman, Fred E. Stafford and Jean Drowart, *J. Chem. Phys.*, **33**, 1784–1789, December 1960.

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344. Scattering of Metastable Helium Atoms in Helium, Neon and Argon.
Articles by G. M. Smith and E. E. Muschlitz, Jr., *J. Chem. Phys.*, **33**, 1819–1825, December 1960.

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345. Diffusion Coefficients of Helium in Fused Quartz.
A masspectrometer was used to study the diffusion of helium through the walls of high purity fused quartz. Diffusion, permeation and solubility rates are given for the temperature range 24° to 1034°C. A. G.

D. E. Swets, R. W. Lee and R. C. Frank, *J. Chem. Phys.*, **34**, 17–22, January 1961.

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346. Dependence of Calculated and Experimental Propane Mass Spectra upon Electron Voltage.
Article by Edward M. Eyring and Austin L. Wahrhaftig, *J. Chem. Phys.*, **34**, 23–28, January 1961.

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347. Low-Temperature Chemisorption. I. Flash Desorption of Nitrogen.
Article by Gert Ehrlich, *J. Chem. Phys.*, **34**, 29–38, January 1961.

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348. Low-Temperature Chemisorption. II. Flash Desorption of Carbon Monoxide.
Article by Gert Ehrlich, *J. Chem. Phys.*, **34**, 39–46, January 1961.

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349. Condensation Coefficients in the Growth of Cadmium and Zinc from the Vapor.
Studies have been made of condensation coefficients in the growth of zinc and cadmium from the vapor phase. The vacuum apparatus used to obtain pressures as low as 10^{-9} mmHg is described.

R. A. Rapp, J. P. Hirth and G. M. Pound, *J. Chem. Phys.*, **34**, 184–188, January 1961.

41. Metals and Alloys

41 : 37 : 21

350. Melting in the Electron Beam Furnace.
G. Ogiermann, *Vacuum*, **10**, 454–465, 1960.

41 : 37

351. Vacuum Casting of Steel.
Belgium. The open hearth steel plant at Seraing is equipped with a Leybold installation for vacuum casting of steel. Vacuum casting is carried out in two different ways: for heavy forging ingots: the degassing takes place directly when pouring steel into the ingot mould; for small forging ingots: the degassing is obtained when transferring steel from the tapping ladle to another ladle; then steel is air-cast. The hydrogen content of the liquid degassed steel is of the order of 2 to 3 $cm^3/100$ g. The cracks initiated by the oxidized inclusions completely disappear thanks to the vacuum casting technique. Elongation and reduction in area are improved; as well, the impact values recorded from transverse radial test specimens. This technique is therefore particularly beneficial to heavy stressed forgings. (Authors)

J. Levaux and L. Hannon, *Vacuum*, **10**, 435–443, 1960.

41 : 21

352. Vacuum Techniques and Metal Properties.
L. Habraken, *Vacuum*, **10**, 412–434, 1960.

41 : 37 : 21

353. Le Traitement sous Vide des Métaux et de l'Acier en particulier.
W. Armbruster, *Vacuum*, **10**, 405–411, 1960.

41 : 22

354. A Method for Measuring of Caesium Vapour Pressure in Photoelectric Tubes.

Yugoslavia. A simple method for determination of caesium vapour pressure (P_{Cs}) in the 10^{-4} to 10^{-15} Torr range based on the surface ionization of caesium on hot tungsten has been described and its theory and accuracy have been discussed. The continuous ion current method allows the determination of P_{Cs} in the (10^{-4}–10^{-9}) Torr range whilst the discontinuous flashing method extends this range from 10^{-9} down to 10^{-15} Torr. The latter method enables the determination of very low residual P_{Cs} in photoelectric tubes. Construction details of various photocells and 11-stage photomultipliers with built-in ionization diodes and electrical circuits used are given. Usefulness of the method is illustrated by following the process of caesium bonding by antimony and silver oxide surfaces and of the adsorption of caesium on glass. (Authors)

S. Jerič and E. Kansky, *Vacuum*, **10**, 234–239, 1960.

41 : 47 : 33

355. Effects of Continuous Gas Clean-up upon Cathodes Emission and Cathode Interface Impedance.

Emission capabilities of oxide cathodes have been studied for many years using techniques of increasing refinement. With the ASTM Standard diode it has been possible to detect significant differences between nickel base alloys and even between heats of these alloys. Results, however, have not been reproducible between laboratories, nor sufficiently sensitive for present-day needs. Study of data indicated the existence of an uncontrolled variable. This has been demonstrated to be gas which evolved slowly and in minute quantities. Gas accumulation in the cathode base metal has been measured. Gas liberation from grid and anode films has been shown to influence emission. Continuous clean-up of gas during tube operation has been shown beneficial. Experiments are being run with a variety of continuous getters, and with continuous pumping. In addition to longer electrical life, there is greater uniformity of cathode emission between readings. Important and unexpected influence upon cathode interface impedance has been found. It will be shown that several advances in tube performance, and simplifications in tube materials may be obtained through control of the micro-amounts of gas liberated continuously during tube life.

Thomas H. Briggs and Stuart Nadeau, *Vacuum*, **10**, 112–117, 1960.

41

356. Kinetics of the Oxidation of Pure Tungsten from 500° to 1300°C.

Kinetic studies were made on the oxidation of tungsten from 500° to 1300°C for time periods up to 6 hr, and for oxygen pressures from 0.1 atm to 0.00132 atm. The rate data were fitted to the parabolic rate law. A number of deviations and transitions were observed. For all of the experiments the initial slopes of the parabolic rate law plots were smaller than the final values found for thick films. A transition in the rate of oxidation was observed for weight gains of 2500/4000μg/cm^2 at temperatures of 650°–800°C. Photographs of the oxidized surface above 650°C show that oxidation occurs in a preferential manner at the edges. Pressure had a strong effect on the rate of oxidation for the experiments above 950°C. At 1200°C the weight loss curves were observed for pressures as high as 0.1 atm. Above 1200°C the oxidation reaction is similar to the combustion of graphite. The rate of oxidation is limited by the volatility of WO_3, the diffusion of oxygen to the surface, and the diffusion of W_3O_9 away from the surface. (Authors)

E. A. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.*, **107**, 619–628, July 1960.

41

357. On the Vacuum Sintering of Tungsten Ingots.

A furnace for vacuum sintering tungsten is described, and results obtained from tungsten sintering experiments are discussed. The rate of densification at various temperatures is given special emphasis, but microstructure, hardness, fabricability, and purity are also examined. Temperatures from 1800° to 3100°C and times from 0.25 to 8.00 hr were employed. Results indicate that sintered densities at least as high as 82.5 per cent of theoretical density are necessary for successful fabrication, and that densities as high as 97.0 have structures which are readily fabricable. High-temperature vacuum sintering is found to produce very pure tungsten, commensurate in this respect with the best arc cast tungsten. (Authors)

J. W. Pugh and L. H. Amra, *J. Electrochem. Soc.*, **107**, 990–993, December 1960.

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358. The Vapor Pressure of Antimony by the Torsion–Effusion Method.

Article by Gerd M. Rosenblatt and C. Ernest Birchenall, *J. Chem. Phys.*, **35**, 788–794, September 1961.

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359. Effect of Chemisorbed Hydrogen on the Magnetization of Nickel.

Article by R. E. Dietz and P. W. Selwood, *J. Chem. Phys.*, **35**, 270–281, July 1961.

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Gettering Activity of Zr, Ti and Ba for Oxygen Gas under the Mercury Vapour. See Abstr. No. 244.

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The Adsorption of Methane by Barium Films in the Presence of a Thermionic Current. See Abstr. No. 249.

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Carbon Monoxide Sorption by Barium Films. See Abstr. No. 250.

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Nitrogen Sorption by Barium Films. See Abstr. No. 251.

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Structure of Barium Getter Films. See Abstr. No. 283.

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Study of the Surface Structure of Barium Getter Deposited Film by an Electron Microscope. See Abstr. No. 284.

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Experience in Designing and Manufacturing All-Metal Vacuum Systems. See Abstr. No. 299.

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Adhesion of Evaporated Metal Films. See Abstr. No. 305.

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A Thin Film Resistor for Measuring Strain. See Abstr. No. 306.

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The Structure and Density of Iron Films formed by Thermal Evaporation. See Abstr. No. 307.

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42. Glass, Ceramics and Refractory Oxides

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The Breakage of Glass Ampoules during Freeze-drying. See Abstr. No. 321.

43. Plastics and Elastomers

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Vacuum Treatment of Molten Steel—a New Way of Improving Converter Steel Production. See Abstr. No. 324.

44. Waxes, Lubricants, Cements, Lacquers, Paints, Oils

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360. Finishing Cosmetic Cases Risdon Creates High-Style, Quality-Controlled Finishes.
Industrial Finishing, 71–72, August 1961.

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361. To Get Better Results in Spray Finishing.
Industrial Finishing, 74–76, September 1961.

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362. Good Design Simplifies Decorative Painting of Molded Plastics.
F. Borries, *Industrial Finishing*, 43–44, October 1961.

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363. Paint as an Engineering Material for Plastic Business Machine Parts.
Other aspects of painting and metallizing of plastics are also discussed.

T. E. Heyden, *Metal Finishing*, No. 7, 49–52, **59**, July 1961.

46. Glass Blowing, Glass-to-metal and Ceramic-to-metal Sealing Techniques

46

364. The Use of Aluminosilicate Glasses in Experimental Vacuum Devices.
The use of these high-melting glasses for vacuum tubes has been described in the literature from time to time. These glasses permit bake-out at temperatures on the order of 700°C and are thus competitive to ceramics as envelope materials. The authors of this report describe some of the techniques which they applied with success to the handling of these glasses, i.e. minimizing reboil by passing the burner gases over a wick saturated with ethyl-orthosilicate, protecting molybdenum pins used for lead wires, by chromallizing and thus avoiding oxidation during sealing at 1200–1300°C, or using oxidation-resistant metals, such as Sylvania No. 4 alloy (42 Ni/5.7 Cr/Bal Fe) in the form of Houskeeper seals.

G. W. Hees and K. D. Earley, *Sylvania Technol.*, **13**, 148–150, October 1960.

46 : 33 : 42

Design Approaches for Electron Devices Operating in Critical Environments, Especially Ceramic-envelope Tubes for High-temperature Operation. See Abstr. No. 318.

47. Outgassing Data, Vapour Pressure Data, Gettering Data

47 : 21

365. Properties of a Small Titanium-Ion Pump.
Germany. A small getter-ion pump is described which has a capacity of several Torr liters for chemically active gases. The maximum pumping speed for CO is about 50 l/sec. The lowest pressure obtained with this pump is less than 10^{-10} Torr. The composition of the residual gases during the process of evacuation has been measured. The factors determining the lowest pressure that can be obtained are discussed. (Authors)

A. Klopfer and W. Ermrich, *Vacuum*, **10**, 128–132, 1960.

47

366. The Influence of Residual Gas on the Performance of the British Post Office Submarine Telephone Repeater Valve Type 6P12.
United Kingdom. The main source of gas in a pentode valve which has been pumped in accordance with the best modern practice has been found to be the occluded gas evolved from the valve components during the manufacture and life of the valve. The virtual elimination of this gas from certain of the valve components prior to valve assembly is one of the chief factors that have permitted the development of passive core valves suitable for use in submarine telephone schemes. (Author)

R. W. Lawson, *Vacuum*, **10**, 100–105, 1960.

47 : 41 : 22

367. Measurement of Gas Evolution and Absorption from Materials used in Vacuum Tubes.
Japan. As a first step of their study on the gas-evolution from materials used in vacuum tubes, the writers took up three methods of measuring in common use, namely, the gas accumulation, the gas flow (differential Pirani gauge) method, and the flow-meter method. The writers, while reviewing the principles of these methods, discussed their sensitivities in relation to various gases, and mentioned difficulties in experimenting with low pressure gases, especially the outgas from the glass wall and other parts of the vacuum system as well as the reaction between the sample material and the gases evolved from it. On the basis of the experimental results, the writers have developed the gas evolution and adsorption gauges on the gas flow method, which record the measurement automatically. Some examples of the actual measurement of outgas characteristics of metal plates are given in this report. The characteristics of the gas absorption of titanium has many interesting problems and it suggests useful applications in the field of the vacuum tube production. The writers also carried out the experiment for studying the gas absorption rate of titanium for such gases as nitrogen, oxygen, carbon mon- and dioxide, at various temperatures. The pressure of the gas sealed in a vessel and contacted with the titanium surface decreased exponentially with time in the pressure range of this experiment, and then it is concluded that the absorption speed is nearly constant. From its dependence the activation energies of absorption for these gases were calculated. Moreover, some interesting phenomena such as the hysteresis effect of gas absorption and the jump of speed which occurred abruptly in the process of the carbon dioxide absorption were found. (Authors)

Kazuji Hashimoto, Hideo Iwayanagi and Hiroshi Fukushima, *Vacuum*, **10**, 92–99, 1960.

47 : 16 : 36 : 20

368. System Design and the Choice of Materials for the "Nimrod" Vacuum System.
United Kingdom. The backbone of a proton synchrotron is the

massive electro-magnet which keeps the protons in orbit. Economy and utility in the design of this in conjunction with the beam dynamics of the machine decide many physical constants of the vacuum system if optimum performance is to be obtained, and the scattering effect of the residual gas molecules on the proton beam determines the pressure at which the system must work. The dimensions of the vacuum vessel are thus determined; calculations relating duct size to pumping speed and gas evolution rate have been carried out and the results of these are presented. Pumping units using 60 cm diameter oil vapour diffusion pumps have been designed and are now being produced. Tests of the first ones show that they are capable of attaining ultimate pressures (with no gas load) of 3×10^{-7} Torr. During investigations to discover the most suitable material with which to make the vacuum vessel, determinations of the gas evolution rates of various polymers have been carried out and certain of the epoxy resins with glass-fibre reinforcement are the best materials so far found, partly because of their high strength to volume ratio. Work has been done to show the effect that irradiation has on the mechanical strength and gas evolution rate of these materials. Techniques are being developed to produce laminates in the workshop which are free from voids that may cause leakage. The gas evolution rates obtained from these epoxy resins are higher than can be tolerated if the requisite operating pressure of 10^{-6} Torr is to be maintained in the vacuum vessel and it is necessary to mask the surface exposed to the vacuum in order to reduce the amount of gas evolved, a technique which has already been applied in the "Saturn" proton synchrotron at Saclay using stainless steel strip, but the different design parameters of "Nimrod" calls for different techniques and considerable attention is being given to this. (Author)

S. H. Cross, *Vacuum*, **10**, 86–91, 1960.

47

369. Degassing of Liquids for Nuclear Spin-Lattice Relaxation Studies.
Note by J. Lees, B. H. Muller and J. D. Noble, *J. Chem. Phys.*, **34**, 341–342, January 1961.

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Electrical Clean-up of Gases in Hot Cathode Discharge Tubes. See Abstr. No. 231.

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Emploi du Spectromètre de Masse dans la Technologie des Tubes Électroniques. See Abstr. No. 236.

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Some Reactions of Water in Electron Tubes. See Abstr. No. 240.

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The Action of Molybdenum, Tungsten, Tantalum and Nickel on Residual Gases in a Vacuum System. See Abstr. No. 255.

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Clean Surfaces and Sorption of Gases. See Abstr. No. 256.

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Experience in Using Mass-Spectrometric Methods in Electro-Vacuum Technology. See Abstr. No. 296.

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Effects of Continuous Gas Clean-up upon Cathodes Emission and Cathode Interface Impedance. See Abstr. No. 355.

48. Heating, Refrigeration, Ultrasonics, Centrifuging

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370. Design Considerations for Vacuum Metallurgical Equipment. *United Kingdom.* The paper discusses some of the more important considerations to be made in the design of vacuum metallurgical equipments. Comparisons of four types of vacuum pump are made relative to capital cost and efficiency in operation. Design of other components relevant to the operating efficiency of a vacuum system are enumerated and particular reference is made to the design of vacuum induction and resistance heated furnaces.

M. E. Harper and W. J. Smith, *Vacuum*, **10**, 444–453, 1960.

49. Miscellaneous Materials and Techniques

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371. A Ferrous Fluoborate Iron Plating Application for Microwave Tubes.
An improved method is described for electroplating iron on tungsten travelling wave tube components to provide attenuation of rf energy. A ferrous fluoborate plating bath is used for this purpose; it involves problems in bath maintenance, pitting, and loss of throwing power. The study of these problems and the corrective techniques that were developed are discussed. (Authors)

C. Zabel and E. Flores, *Sylvania Technol.*, **13**, 97–100, July 1960.

49

372. Vaporization of Aluminum Arsenide.
Article by Michael Hoch and Kamalakar S. Hinge, *J. Chem. Phys.*, **35**, 451–453, August 1961.

49

373. Thermodynamics of the Vaporization of Nickel Oxide.
Article by R. T. Grimley, R. P. Burns and Mark G. Inghram, *J. Chem. Phys.*, **35**, 551–554, August 1961.

49

374. Solid-Film Molybdenum Disulphide Lubricants.
Article by E. B. Palmer, *Materials in Design Engineering*, **54**, 122–126, August 1961.

49

375. Electrical Conductivity of Synthetic Crystalline Zeolites.
Article by Donald C. Freeman, Jr. and Dennis N. Stamires, *J. Chem. Phys.*, **35**, 799–806, September 1961.

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Basic Science and Engineering

51. Physics, Astonomy, Geophysics

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376. Powerful Tool: Statistical Mechanics.
Article by John S. Dahler, *Chemical Engineering*, **68**, No. 1, 111–118, January 9, 1961.

54. Biology, Biochemistry, Pharmaceutics, Toxicology, Organic Chemistry

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377. Note on Vacuum and Condensing Temperature Requirements for the Freeze-Drying of Tissue.
S. Cotson, *Vacuum*, **10**, 266, 1960.

54 : 36 : 38

378. Vacuum in Medicine.
United Kingdom. The authors give a survey of the scope and actual applications of vacuum engineering in the medical field. After remarks on the direct application of suction in the early days of history, the authors discuss the preparation of pharmaceutical materials and in this connexion mention various forms of distillation and freeze-drying. The main part of the article is devoted to an appreciation of the electron microscope and subsidiary techniques such as specimen preparation, the importance of X-rays and technical aspects connected with it as well as the preparation and uses of isotopes. (Authors)
J. Bounden and J. Rotblat, *Vacuum*, **9**, 1–16, 1959.

56. Electrical Engineering, Electronic Circuits, Electrical Devices

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Apparatus for the Controlled Deposition of Optical Film Systems. See Abstr. No. 265.

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Vacuum Deposition of Dielectric Films for Capacitors. See Abstr. No. 304.

Miscellaneous

65. Professional Societies, Committees, Organisations

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The International Organization for Vacuum Science and Technology. See Abstr. No. 221.

V A C U U M

Papers to be published in future issues

K. H. Behrndt and R. W. Love : Automatic Control of Film-deposition Rate with the Crystal Oscillation for Preparation of Alloy Films.

P. White : Gas Phase Oxidation of Silicon Monoxide during Formation of Evaporated Films.

E. E. Donaldson : Particulate Contamination from Glass.

J. K. Gorman and W. R. Nardella : Hydrogen Permeation through Metals.

T. R. A. Davey : Distillation under Moderately High Vacuum, Illustrated by the Vacuum Distillation of Zinc from Lead.

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